Diagnostics of H₂O and H₂O+He Supersonic Jets by Raman Spectroscopy

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Abstract. The stagnation conditions for production of pure H₂O and H₂O+He supersonic jets free of condensation are reported. Number densities and rotational populations of uncondensed H₂O+He jets have been measured by Raman spectroscopy. This diagnostics is aimed at characterizing quantitatively the main flow properties: number densities, rotational and translational temperatures, flow velocity, rotational populations and their gradients along the jet. Combining these data in a Master Equation accounting for the evolution of rotational populations along the jet, a description has been shown feasible in terms of average rate coefficients for inelastic collisions, a novel concept which simplifies considerably the molecular interpretation of non-equilibrium and relaxation. Experimental average rates for H₂O:He inelastic collisions are in the range of 340 to $700 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$, somewhat larger than the corresponding values from *ab-initio* calculations. Rates for H₂O:H₂O inelastic collisions are 4 to 7 times larger than for H₂O:He collisions.

Keywords: Supersonic jets, Water, Helium, Inelastic collisions, Raman spectroscopy

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INTRODUCTION

The experimental study of H₂O supersonic free jets, pure and diluted in He, poses a number of difficulties which are not found in jets of atoms (He, Ne, Ar), diatomic molecules (N₂, H₂, O₂, CO), nor linear triatomic molecules (CO₂). Major problems for the quantitative study of H₂O jets are the sharp tendency to condensation, and the complex structure of H₂O rovibrational spectra due to two independent asymmetric top species with ratio 3:1, *ortho*-H₂O and *para*-H₂O. Therefore, very few data on H₂O supersonic jets can be found in the literature. In this work we report a quantitative study of a number of such jets generated under different stagnation conditions. The study is aimed at establishing their main characteristics, with emphasis on the condensation limits and on the non-equilibrium problems towards future studies of the H₂O:H₂O and H₂O:He inelastic collisions, a question of broad scientific and technical interest, and of fundamental importance in present-day molecular astrophysics.

Among the various diagnostic techniques - electron beam fluorescence, laser induced fluorescence, infrared spectroscopy, resonance enhanced multiphoton ionization (REMPI), coherent antistokes Raman spectroscopy (CARS), and spontaneous Raman spectroscopy - only the latter appears to be capable of providing accurate number density and rotational population data with sufficient sensitivity and space resolution along and across the jet. State-of-the-art Raman spectroscopy as described next is, no doubt, a good choice for quantitative studies of H₂O related jets.

INSTRUMENTATION

One of the two jet diagnostics facilities at the Instituto de Estructura de la Materia (CSIC) in Madrid has been employed in this work. It consists of **1**) an expansion chamber connected to **2**) a vacuum line for production of steady supersonic free jets through **3**) a commercial airbrush nozzle fed by a H₂O+He supply line. Raman scattering along selected points of the jet are excited by **4**) a powerful *cw*-laser, being detected by **5**) a high sensitivity Raman spectrometer. Laser source, expansion chamber, and spectrometer are optically connected by means of **6**) a highly efficient transfer optics system. These main elements, and the vacuum system as well, are mounted onto independent structures in order to minimize the effect of vibrations. Nozzle, laser focusing optics, and Raman scattering collection optics inside the expansion chamber are mounted onto high-accuracy ($\pm 1 \mu\text{m}$) xyz-positioning stages operated by remote control.

1. Expansion chamber. Manufactured in welded aluminum, with dimensions of $55 \times 44 \times 59 \text{ cm}^3$ and 3 cm thick walls and 5 cm thick basis, it is coated black inside in order to minimize stray light. Five DN250 and seven DN63 flanges

allow for installation of different parts, pressure sensors, optical windows, gas feeding line, and electrical connections.

2. Vacuum line. It consists of a 2000 l/s turbopump installed on the top of the expansion chamber. A gate valve between the expansion chamber and the turbopump allows for reference static measurements at known absolute number density. The turbopump is backed by a Roots 430 m³/h pump and a 70 m³/h rotary pump. A liquid-N₂ trap in between both pumps condenses the expanded H₂O.

3. Nozzle and H₂O+He supply line. A commercial airbrush nozzle of diameter $D = 350\ \mu\text{m}$ equipped with a three-point active heating closed loop system has been employed. Nozzle tip, nozzle body, and pipe are stabilized at different temperatures in order to maintain a smooth flow gradient, avoiding condensation in the supply line as far as possible. Nozzle operation temperature ranges between 300 and 373 K. Mixtures of accurate molar fractions of H₂O and He at the desired stagnation partial pressure of H₂O are supplied by a Bronkhorst Hi-TEC controlled evaporator mixer combined with mass flow controllers.

4. Laser source. Raman scattering is excited by a Coherent Radiation (Verdi V10) *cw*-laser source providing up to 10 W vertical linear polarized radiation at $\lambda = 532\ \text{nm}$. The 1.8 mm wide laser beam is sharply focused onto the chosen points of the jet by means of an $f = 35\ \text{mm}$ Ar14-coated lens.

5. Spectrometer. The spectrometer is a 1-meter additive double monochromator with two gratings of 2400 l/mm equipped with a CCD detector of 2048×512 pixels size $20\ \mu\text{m}$ refrigerated by liquid N₂. Scanning and data acquisition are computer controlled by means of an *ad-hoc* home developed software (REGISTRA, version 3.02). Representative data acquisition time per Raman spectrum is 60 s. Each data point along the jet requires the average of several spectra, from three to ten, depending on the intensity of the Raman signal.

6. Transfer optics. Raman scattering from selected points along the jet is collected by a 50 mm f/1.1 Leica photographic objective and then projected onto the entrance slit of the spectrometer by a $f = 500\ \text{mm}$ achromat with a $10\times$ total magnification. Spatial resolution of the probed volume element along the jet is determined by the entrance slit width of the spectrometer, and across the jet by the pixel binning system of the CCD detector. Representative values for this work are $15\ \mu\text{m}$ along the jet, and $70\ \mu\text{m}$ across.

7. Micropositioning. Probed points along the jet are selected by moving the nozzle by $100\ \mu\text{m}$ steps while the laser focus and the Raman collection optics remain static. Representative pointing accuracy within the flow field is $\pm 5\ \mu\text{m}$, and repeatability is better than $\pm 1\ \mu\text{m}$.

H₂O+He FREE JETS

Due to the deep well of the H₂O-H₂O intermolecular potential surface ($\approx 1200\ \text{cm}^{-1}$), jets with significant amounts of H₂O are prone to condense, even for source temperatures as high as 370 K and source pressure p_0 as low as 100 mbar. Unlike to other three-atomic molecules like CO₂, where the onset of condensation starts at about the first nozzle diameter downstream from nozzle exit [1], H₂O related jets appear to start condensing inside the nozzle for a wide range of source conditions.

Condensation in CO₂ jets can be easily recognized by the change of curvature of the rotational temperature function $T_r(z)$ at $z/D \approx 1$, and later enhancement of T_r showing a maximum at about $z/D \approx 2$. In addition, CO₂ jets with condensation show clear spectral fingerprints of condensation at 1385 (liquid) and 1384 cm⁻¹ (solid) [1]. Nothing like this is observed in H₂O jets, even for a condensed fraction as high as 50 %. Since condensation in H₂O jets starts inside the nozzle, the $T_r(z)$ function decreases smoothly and does not show any maximum, eventually reaching the asymptotic value $T_{r\infty}$ at some far-downstream region of the jet. Search for spectral features associated with liquid or solid H₂O in the jet proves useless since they are extremely broad ($\approx 800\ \text{cm}^{-1}$) compared with the relatively narrow Q($v = 1$) rovibrational Raman at band at 3657 cm⁻¹ employed as a probe for rotational temperatures and number densities. A practical way of detecting condensation in H₂O jets is by means of the global enhancement of $T_r(z)$ function as a function of stagnation pressure p_0 . It is well established that $T_r(z)$ decreases in uncondensed jets (at fixed position z) with increasing stagnation pressure. So, identification of H₂O jets free of condensation is possible by observing the lower boundary of $T_r(z)$ as a function of p_0 at fixed nozzle temperature. Moreover, a decrease in the observed experimental number density $n(z)$ of the uncondensed phase (H₂O gas) with respect to the theoretical total number density expected from hydrodynamical models for uncondensed gas confirms condensation. Rayleigh scattering intensity enhancement also provides information about condensation in the jet [1].

A summary of several pure H₂O jets casuistry in search for condensation-free conditions is shown in Fig. 1. Jet A was generated through a $D = 280\ \mu\text{m}$ airbrush nozzle, and jets B to G through a similar $D = 350\ \mu\text{m}$ nozzle. Stagnation temperatures were in the range 363 to 374 K. Jets below this thermal threshold did show a significant condensed fraction. Since translational temperatures T_t are relatively insensitive to stagnation pressure, an estimate of

T_t from the isentropic model and parametric description of Mach number [2] for $T_0 = 361.1$ K and $\gamma = 1.333$) is shown as a reference in Fig. 1.

In the absence of condensation, the trend of rotational temperatures $T_r(G) > T_r(F) > T_r(E) > T_r(D) > T_r(C) > T_r(B) > T_r(A)$ should be expected, inversely correlated with stagnation pressures, i. e. with collisional frequency. However, the experiment is in evident contradiction with this pattern. The reversed observed pattern $T_r(A) > T_r(B) > T_r(C) > T_r(D)$ is indicative of massive condensation, since the released condensation energy causes a notorious increment of rotational temperature, among other effects [3]. Condensation clearly decreases from jet A to jet D. Jet E is probably weakly condensed, jet F is probably uncondensed, and condensation in jet G, if any, is not detectable. Rayleigh scattering intensity enhancement confirm semiquantitatively this conclusions. In contrast, low stagnation pressure jets G, F, and E, with $T_r(G) > T_r(F) > T_r(E)$ are in the expected order for uncondensed jets, since $n(G) < n(F) < n(E)$. This indicates little condensation, if any. In any case the degree of possible condensation does not perturb significantly the $T_r(G) > T_r(F) > T_r(E)$ expected pattern for uncondensed jets. Rayleigh scattering, although in the limit of signal to noise ratio is consistent with this conclusion. The behavior of jet D with respect to jet E, with $T_r(D) \approx T_r(E)$, but $n(E) < n(D)$ indicates that jet D, generated at $p_0 \approx 96$ mbar is unambiguously contaminated by condensation. So we can propose with a reasonable degree of confidence the condensation threshold $n_0 \approx 40$ mbar at $T_0 = 363$ K for pure H_2O jets generated through the $D = 350$ μm airbrush nozzle; pure H_2O jets at lower stagnation pressures and higher stagnation temperatures are expected to show negligible condensation for the purpose of collisional studies.

The effect of He onto the condensation of H_2O in H_2O+He mixed jets is not well known. Preliminary studies in H_2+He jets indicate [4] that He in excess, acting as a third body, increases the efficiency of condensation of H_2 by about a factor three. So, one may conjecture that H_2O+He jets generated using the same nozzle at $n_0(H_2O) \leq 13$ mbar and $T_0 \geq 363$ K, should probably be rid from condensation.

Jets A, B, C, D, E, and F were aimed at establishing the condensation-free conditions. Jets F, G, H, I, J (see Table 1), which satisfy the mentioned condensation-free conditions have been studied quantitatively in detail in order to provide the experimental data required for the study of $H_2O:H_2O$ and $H_2O:He$ inelastic collisions based in the procedure described elsewhere [5], and some novel variants introduced in the present work. It employs a Master Equation which describes the evolution of rotational populations along the jets in terms of inelastic collision rates. The input quantities are the number densities, rotational temperatures, rotational populations, and translational temperatures. These quantities have been determined from the experiment for jets F, G, H, I, J as a function of distance to the nozzle.

EXPERIMENTAL DATA

The raw data were measured at steps of 0.1 mm from $z = 0.1$ mm ($z/D = 0.29$) downstream to the nozzle up to $z = 2.4$ mm ($z/D = 6.86$) in jets F, G, H, I, J according to the procedures described next.

Number densities. Since Raman intensity of a vibrational Q-branch is strictly proportional to the local molecular number density $n(z)$, this quantity was measured along the jet by comparison with a static H_2O sample at known number density employing the integrated intensity of the $Q(v_1)$ Raman band at ≈ 3657 cm^{-1} . Raw data depart randomly from a smooth ad-hoc function by less than 3 %. Interpolating between stagnation n_0 , supposed at $z \approx -0.2$, mm and $z \leq 0.8$ mm experimental points, the raw $n(z)$ data obey to very good approximation a function of the form

$$n = n_0 - c_n * \exp(-b_n/(X+1)^{a_n}), \quad (1)$$

for all five F, G, H, I, J jets. Variable $X = z + 1$, for z expressed in units of 0.1 mm, has been chosen for numerical convenience. Parameters a_n , b_n , c_n are different for each jet. Representative accuracy for $n(z)$ smoothed data is better 5 %.

The **rotational temperatures** T_r along the jets were obtained by simulation of the partially resolved rotational structure of the $Q(v_1)$ Raman band of H_2O measured at each data point. Detailed cross-section data [6] were employed for this purpose. In spite of the asymmetric top geometry of H_2O , with three non-degenerated rotational degrees of freedom, the rovibrational profiles could be reproduced within experimental accuracy by using only one rotational temperature. Moreover, the *ortho*- H_2O and the *para*- H_2O species, which are in the ratio 3:1 in *natural*- H_2O , obey the same rotational

temperature within experimental accuracy. A sample spectrum and its simulation is shown in Fig. 2.

FIGURE 1. Rotational temperatures along several jets of H_2O generated at different stagnation pressures.

FIGURE 2. Representative measurement of rotational temperature in a H_2O+He jet

Rotational temperatures measured along the jets obey within great accuracy functions of the type

$$T_r = T_0 - c_r * \exp(-b_r/(X+1)^{a_r}), \quad (2)$$

along the whole range investigated; a_r , b_r , and $c_r = T_0 - T_{r,\infty}$ are parameters to be fitted to the set of experimental data. The T_r 's (raw and smoothed) of pure H_2O jet G, and of the mixed H_2O+He jets H, I, J are shown in Fig. 3. For clarity jet F has been omitted from Fig. 3 since it overlaps substantially with jet H. The parameters for the smoothed T_r 's are given in Table 1, jointly with the standard deviation σ and the R_{sq} coefficient of determination, which quantify the quality of the analytical description with respect to the raw experimental T_r 's. For comparison, translational temperatures T_t of the same jets are shown in Fig. 4.

TABLE 1. Stagnation conditions and T_r best-fit a_r , b_r , c_r parameters (Eq. (2)) of supersonic free jets of pure H_2O and H_2O+He expanded through a $D = 350 \mu m$ airbrush nozzle; T_0 is the stagnation temperature, and P_0 the total (H_2O+He) stagnation pressure; N is the number of T_r raw data points, σ is the *raw-fit* standard deviation, and R_{sq} the coefficient of determination.

jet	T_0/K	$P_0/mbar$	$H_2O(\%)$	$He(\%)$	a_r^a	b_r^a	c_r/K	N	σ/K	R_{sq}
F	362.9	41.5	100	0	1.331	4.055927	295.2	14	0.46	0.9999
G	363.4	11.75	100	0	1.364	4.061995	215.5	24	3.54	0.9863
H	363.1	57.4	34	66	1.443	4.196256	287.5	26	0.86	0.9995
I	363.0	190	6.5	93.5	1.656	5.140830	318.6	26	1.17	0.9992
J	361.3	320	3.3	96.7	1.582	4.082052	332.1	26	0.79	0.9996

^a fractional units for dimensionless exponent in Eq. (2)

The jets G, H, I, J are in the range of partial pressures of H_2O between 12 and 20 mbar. The intensity of the Raman spectra should therefore differ among them by less than a factor two, and the standard deviation σ by less than $\sqrt{2}$. This is indeed the case for jets H, I, J, but not for jet G of pure H_2O , which shows a much higher T_r raw-data dispersion. This is due to the difficulty to maintain a stable jet of pure H_2O at such low stagnation pressure without using a driving flow of He carrier gas in the controlled H_2O evaporator mixer. With this limitation, the $\sigma \approx 1$ K of jets H, I, J shows the high quality of the T_r data. The $R_{sq} \approx 1$ value found in all cases confirms that the empirical functional description of T_r after Eq. (2) is indeed very good. No theoretical reasons for such accuracy are known at present.

The **rotational populations** $P_i(z)$ for *ortho*- H_2O and *para*- H_2O were obtained from the simulation of the individual rotational lines within the $Q(v_1)$ Raman band for the best-fit T_r . The rotational populations of the lowest energy levels

of the jets investigated do not depart significantly from a Boltzmann distribution at the temperature T_r of Fig. 2. The evolution of rotational populations along a representative jet is shown in Figs. 5 and 6.

Translational temperatures T_t along the jet can not be obtained to date by direct measurement. However they can be obtained indirectly by combining the $n(z)$ and $T_r(z)$ experimental data and the conservation of mass, momentum, and energy according to the procedure described elsewhere [3]. Translational temperatures are well described by the functional form of Eq. (2).

Local **flow velocities** $v(z)$ were obtained from T_r and T_t by means of the conservation of energy. For $\text{H}_2\text{O}+\text{He}$ mixed jets with mole fraction α of H_2O it leads to

$$v^2 = \frac{R}{\langle W \rangle} (5(T_0 - T_t) + 3\alpha(T_0 - T_r)), \quad (3)$$

where $R = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$ is the universal gas constant, and $\langle W \rangle = \alpha W(\text{H}_2\text{O}) + (1 - \alpha)W(\text{He})$ the average molar mass of the expanded gas.

Time derivatives dP_i/dt along the jets were obtained from the gradients dP_i/dz and the local flow velocity through the relation $dP_i/dt = v dP_i/dz$.

FIGURE 3. Rotational temperatures along $\text{H}_2\text{O}+\text{He}$ jets.

FIGURE 4. Translational temperatures along $\text{H}_2\text{O}+\text{He}$ jets.

MOLECULAR INTERPRETATION OF JETS

The strong non-equilibrium between rotational and translational temperatures along the jets shown in Figs. 3 and 4 can be interpreted in terms of inelastic collisions employing a Master Equation (MEQ) of the generic form

$$dP_i/dt = n \sum_l (-P_i k_{i \rightarrow l} + P_l k_{l \rightarrow i}), \quad (4)$$

which accounts for the time evolution of the population P_i of the rotational level i of H_2O as a consequence of inelastic collisions with an He atom; n is the total number density, and the molecular species is supposed to be infinitely diluted in He; $k_{i \rightarrow l}$ is the state-to-state inelastic rate for the transition $i \rightarrow l$ induced by an $\text{H}_2\text{O}:\text{He}$ inelastic collision in the gas at translational temperature T_t ; $k_{i \rightarrow l}$ and $k_{l \rightarrow i}$ rates are related by detailed balance. For practical reasons it is convenient

to label the energy levels by increasing energies, starting with index $i = 1$ for the lowest energy, as shown in the insets of Figs. 5 and 6.

FIGURE 5. Population of the eight lowest rotational levels of *para*-H₂O along the H₂O(3.3%)+He(96.7%) free jet through a $D = 350 \mu\text{m}$ airbrush nozzle; $p_0 = 320 \text{ mbar}$, $T_0 = 361.3 \text{ K}$.

FIGURE 6. Population of the eight lowest rotational levels of *ortho*-H₂O along the H₂O(3.3%)+He(96.7%) free jet through a $D = 350 \mu\text{m}$ airbrush nozzle; $p_0 = 320 \text{ mbar}$, $T_0 = 361.3 \text{ K}$.

As has been shown elsewhere [7], Eq. (4) can be reduced to the system

$$\begin{aligned}
 dP_1/dt &= a_{21}k_{2 \rightarrow 1} + a_{31}k_{3 \rightarrow 1} + \cdots + a_{r1}k_{r \rightarrow 1} + \cdots, \\
 dP_2/dt &= -a_{21}k_{2 \rightarrow 1} + a_{32}k_{3 \rightarrow 2} + \cdots + a_{r2}k_{r \rightarrow 2} + \cdots, \\
 &\vdots = \vdots, \\
 dP_m/dt &= -a_{m1}k_{m \rightarrow 1} - a_{m2}k_{m \rightarrow 2} + \cdots + a_{m+1,m}k_{m+1 \rightarrow m} + \cdots,
 \end{aligned} \tag{5}$$

expressed in terms of only *down* rate coefficients. The system (5) can also be expressed in the general form

$$dP_i/dt = - \sum_{r < i} a_{ir}k_{i \rightarrow r} + \sum_{s > i} a_{si}k_{s \rightarrow i}, \tag{6}$$

with coefficients

$$a_{ir} = n \left(1 - \exp \left[-(\epsilon_i - \epsilon_r) (T_i^{-1} - T_r^{-1}) \right] \right) P_i, \text{ for } r < i, \tag{7}$$

and

$$a_{si} = n \left(1 - \exp \left[-(\epsilon_s - \epsilon_i) (T_i^{-1} - T_r^{-1}) \right] \right) P_s, \text{ for } s > i, \tag{8}$$

where $\epsilon_i = \beta E_i$ is the energy of the rotational level i expressed in Kelvin; $\beta = 1.4388 \text{ K/cm}^{-1}$ is the conversion factor from energies E_i in cm^{-1} to ϵ_i in K. The coefficients a_{ir} and a_{si} are a function of number density n , rotational populations P , and rotational and translational temperatures T_r and T_i , and can thus be obtained from the experiment, as well as the dP/dt left-hand-terms in Eqs. (5) or (6). Note that the exponent in Eqs. (7) and (8) account for the $T_r \neq T_i$ non-equilibrium, and depend on the difference of energies between the pre-collisional and post-collisional rotational states.

State-to-state rate coefficients $k_{i \rightarrow r}$ or $k_{s \rightarrow i}$ can not be obtained in general from the experiment, since their number exceeds by far the number of available equation. However, an useful concept which accounts for the efficiency of inelastic collisions is the average (down) rate coefficient for rotational level i , defined as

$$\langle k_{s \rightarrow i} \rangle_{s > i} = \frac{dP_i/dt + \sum_{r < i} a_{ir} \langle k_{i \rightarrow r} \rangle}{\sum_{s > i} a_{si}}. \tag{9}$$

Physically it represents the weighted average value of the state-to-state (down) rate coefficients $k_{s \rightarrow i}$ for the levels of energy $E_s > E_i$. The $\langle k_{s \rightarrow i} \rangle$'s for the rotational levels sufficiently populated can be obtained from the experiment following an iterative procedure which starts with $i = 1$ and takes into account that $\langle k_{1 \rightarrow r} \rangle_{r < 1} = 0$. The $\langle k_{s \rightarrow i} \rangle$'s are not strictly jet-invariant as they depend on the actual rotational populations, but they differ little if the stagnation number densities of the molecular species in the jets are within the same order of magnitude, and the stagnation temperatures are similar. The $\langle k_{s \rightarrow i} \rangle$'s provide a practical estimate of the efficiency of inelastic collisions which affect a particular energy level. An additional advantage is that they can also be calculated for a particular jet from the individual state-to-state rates $k_{s \rightarrow i}$ from *ab-initio* calculations (if available) by means of

$$\langle k_{s \rightarrow i} \rangle_{s > i} = \frac{\sum_{s > i} a_{si} k_{s \rightarrow i}}{\sum_{s > i} a_{si}}, \quad (10)$$

which provides an experimental test for the quality of *ab-initio* calculations algorithms, or for the potential energy surfaces employed in them.

The theory presented so far refers to jets with infinite molecular dilution in atoms. This condition can not be attained in the present experiments, where the highest dilution of H₂O in He compatible with a sufficient signal to noise is 3.3 % (jet J). This can be overcome by generalizing Eqs. (4) to a linear combination for the H₂O+He mixture involving α molar fraction of H₂O, and $(1 - \alpha)$ molar fraction of He. The generalized Eqs. (5) include the $\langle h_{s \rightarrow r} \rangle$'s for the H₂O:H₂O inelastic self-collisions, and the $\langle k_{s \rightarrow r} \rangle$'s for the H₂O:He hetero-collisions.

Combining the experimental data from F, G (pure H₂O) and H, I, J (H₂O+He) jets, the average rate coefficients $\langle h_{s \rightarrow r} \rangle$'s for the H₂O:H₂O, and the $\langle k_{s \rightarrow r} \rangle$'s for the H₂O:He collisions have been determined. The results for $T_t = 40$ K are shown in Table 2, jointly with the corresponding values from *ab-initio* calculations for H₂O:He inelastic collision rates [8,9].

TABLE 2. Average $\langle k_{s \rightarrow i} \rangle$ and $\langle h_{s \rightarrow i} \rangle$ (down) rates for *ortho*-H₂O:He and H₂O:H₂O inelastic collisions at $T_t = 40$ K as obtained from experiment, and from *ab-initio* calculations. Label i stands for the six lowest rotational energy levels of *ortho*-H₂O given in Fig. 6. Rates are in units of $10^{-20} \text{ m}^3 \text{ s}^{-1}$.

Level i	average rate $o\text{-H}_2\text{O:He}$	<i>ab-initio</i> from [8] Eq. (10)	<i>ab-initio</i> from [9] Eq. (10)	exptl Eq. (9)	average rate H ₂ O:H ₂ O	exptl Eq. (9)
1	$\langle k_{s \rightarrow 1} \rangle$	527 ± 71^a	696 ± 92^a	689 ± 28^b	$\langle h_{s \rightarrow 1} \rangle$	2411 ± 98^b
2	$\langle k_{s \rightarrow 2} \rangle$	400 ± 50	507 ± 62	536 ± 11	$\langle h_{s \rightarrow 2} \rangle$	2144 ± 44
3	$\langle k_{s \rightarrow 3} \rangle$	542 ± 50	746 ± 51	584 ± 19	$\langle h_{s \rightarrow 3} \rangle$	2920 ± 76
4	$\langle k_{s \rightarrow 4} \rangle$	293 ± 3	347 ± 8	341 ± 31	$\langle h_{s \rightarrow 4} \rangle$	2387 ± 217
5	$\langle k_{s \rightarrow 5} \rangle$	540 ± 20	667 ± 29	490 ± 50	$\langle h_{s \rightarrow 5} \rangle$	3430 ± 350
6	$\langle k_{s \rightarrow 6} \rangle$	375 ± 11	496 ± 11	503 ± 29	$\langle h_{s \rightarrow 6} \rangle$	3521 ± 203

^a uncertainties arise from a_{si} coefficients in Eq. (10) for the jets H, I, J

^b uncertainties arise from dP_i/dt data and a_{si} coefficients in Eq. (9) for the jets H, I, J

Table 3 shows the recalculated values of dP_i/dt 's using the experimental average rates $\langle k_{s \rightarrow i} \rangle$ and $\langle h_{s \rightarrow i} \rangle$ of Table 2, which are common to three different H₂O+He jets. The overall agreement for the fairly different flow conditions of these three jets proves the value of the average rate concept, Eqs. (9) and (10), for the interpretation of jets in molecular terms.

DISCUSSION AND CONCLUSIONS

One of the main difficulties for the study of H₂O:H₂O and H₂O:He inelastic collisions in supersonic jets arises from the strong tendency of H₂O to condense in jets. Since cluster:molecule collisions strongly bias the flow properties of the jets, a rigorous study of H₂O:H₂O and H₂O:He collisions must be based on jets free of condensation. To worsen things, the condensed phase (clusters, droplets) of H₂O in jets is difficult to identify spectroscopically, since the spectral fingerprint of the condensed phase is over 800 cm^{-1} broad, with no clear identifiable features. This is at least 80 times broader than the $Q(v_1)$ branch of the gas phase at rotational temperatures below 150 K. Therefore, H₂O condensation as high as 50 % is hardly observable in the Raman spectra. Only indirect methods, like the enhancement of rotational temperature of the uncondensed H₂O fraction with increasing stagnation pressure, or the corresponding

TABLE 3. Time evolution dP_i/dt of populations of *ortho*-H₂O rotational levels at $T_i = 40$ K positions of H₂O+He jets H, I, and J as measured and as recalculated with the experimental average (down) rates from Table 2, columns 5 and 7; dP_i/dt 's are in units of 10^3 s^{-1} . Experimental accuracy is better than 10 %

Jet → <i>i</i> -level	dP_i/dt					
	34%H ₂ O+66%He		6.5%H ₂ O+93.5%He		3.3%H ₂ O+96.7%He	
	exptl	recalc	exptl	recalc	exptl	recalc
1	80	79	291	305	419	406
2	48	47	142	146	165	164
3	21	20	7	3	-54	-49
4	-10	-10	-62	-67	-100	-98
5	-14	-14	-87	-82	-139	-135
6	-19	-20	-76	-77	-93	-97

enhancement of Rayleigh scattering intensity, prove useful to detect condensation. This has been done in the first part of the present work for a wide range of source conditions in pure H₂O and H₂O+He mixed jets. We conclude that

- 1) Pure H₂O jets expanded through $D \geq 350 \text{ } \mu\text{m}$ nozzles at stagnation temperatures $T_0 \geq 363 \text{ K}$ show negligible condensation for stagnation pressure $p_0 \leq 40 \text{ mbar}$.
- 2) H₂O+He jets expanded through $D \geq 350 \text{ } \mu\text{m}$ nozzles at stagnation temperatures $T_0 \geq 363 \text{ K}$ show negligible condensation for stagnation partial pressure $p_0(\text{H}_2\text{O}) \leq 13 \text{ mbar}$, regardless of the abundance of He.

Several H₂O and H₂O+He jets satisfying the above conditions have been characterized quantitatively in order to provide data for the study of H₂O:H₂O and H₂O:He inelastic collisions. Number densities, rotational and translational temperatures, flow velocities, and gradients of rotational populations of *ortho*-H₂O and *para*-H₂O have been obtained with unprecedented accuracy by Raman spectroscopy diagnostics. Combining such data in a Master Equation accounting for the evolution of rotational populations along the jets, much information has been obtained on the H₂O:H₂O and H₂O:He inelastic collision rates. The concept of averaged (down) rate coefficient associated with a particular rotational level has been introduced here for the first time. It proves useful to synthesize the global influence of the many state-to-state rates involved in the interchange of energy between translational and rotational degrees of freedom. We have found that

- 3) Experimental $\langle k_{s \rightarrow i} \rangle_{s>i}$ average rates for *ortho*-H₂O:He inelastic collisions at $T_i = 40 \text{ K}$ are up to 35 % larger than the corresponding ones calculated by *ab-initio* methods [8], but in better agreement with a recent calculation [9]. See Table 2 for details.
- 4) Experimental $\langle h_{s \rightarrow i} \rangle_{s>i}$ average rates for H₂O:H₂O inelastic collisions at $T_i = 40 \text{ K}$ are four to seven times larger than the corresponding rates for *ortho*-H₂O:He collisions. See Table 2 for details. This result is in marked contradiction with theoretical estimates which predict values up to two orders of magnitude larger [10].
- 5) The results on Table 3 prove that the time evolution dP_i/dt of rotational populations in three fairly different H₂O+He jets can be described to better than 10 % with a common set of $\langle k_{s \rightarrow i} \rangle_{s>i}$ and $\langle h_{s \rightarrow i} \rangle_{s>i}$ averaged rates.

Present results show the feasibility of a molecular interpretation of relaxation in supersonic jets involving H₂O molecules. The wide thermal range of the present experiments, shown in Figs. 3 and 4, and the rotational populations shown in Figs. 5 and 6, suggests the possibility of obtaining $\langle k_{s \rightarrow i} \rangle_{s>i}$ and $\langle h_{s \rightarrow i} \rangle_{s>i}$ averaged rates at least between $T_i = 20$ and 100 K not only for *ortho*-H₂O:He but also for *para*-H₂O:He collisions. Whether *ortho*-H₂O:*ortho*-H₂O, *ortho*-H₂O:*para*-H₂O and *para*-H₂O:*para*-H₂O collisions can be studied in detail with the present data is still under evaluation.

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