Raman Spectroscopic Experiments on Boltzmann Collision Integral in Supersonic Jets

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Abstract. State of the art Raman spectroscopy adapted to quantitative investigation of gasdynamic problems in supersonic jets is reported. The facilities employed in these experiments are based on high spatial resolution ($< 5\mu\text{m}$) and high-sensitivity spectroscopy (< 1 photon/sec), providing us with absolute number density and rotational population data of unprecedented accuracy in a wide range of conditions. Data from the zone of silence of the jet are combined with the state-to-state collisional rates in the frame of a master equation derived from Boltzmann collision integral, leading to a detailed understanding of the underlying physics of relaxation, and of nucleation kinetics in terms of the most elementary collision processes.

Keywords: Raman spectroscopy, Instrumentation, Supersonic jets, Boltzmann equation, Relaxation, Condensation

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INTRODUCTION

The micro- and macroscopic formulations of gas dynamics rest upon Boltzmann equation. Originally formulated in 1872 for structureless particles it was generalized later for molecules with internal degrees of freedom [1-3]. Boltzmann equation remains today the cornerstone of rarefied gas dynamics, providing the basis for macroscopic equations, transport coefficients, and microscopic information on collisions, which are the elementary processes underlying the whole problem.

Supersonic jets are gas dynamic quasi-universal structures showing a wealth of features combining laminar and turbulent flow, relaxation effects, shock waves, vortices, slip effects, and condensation, spanning a wide range of densities, temperatures, chemical species, and Kn numbers. Since supersonic jets can be generated in the laboratory under different stagnation conditions, they provide a manageable medium to work experimentally on Boltzmann equation. Among the experimental methods in gas dynamics, state of the art Raman spectroscopy occupies a privileged position for the mentioned purpose.

Recent results on rarefied gas problems in supersonic jets, obtained through Raman spectroscopy are presented next, keeping in mind that the ultimate goal of such experiments is to connect the micro- and macroscopic approaches of gas dynamics, with particular emphasis on Boltzmann collision integral.

RAMAN SPECTROSCOPY

Raman scattering is a two-photon inelastic process which provides the basis for one of the most powerful non-intrusive diagnostic techniques ever developed. It is useful in a wide scope of problems in virtually all branches of science where molecules are relevant. Applications in chemistry, physics, material science, biology, geology, art, combustion, atmospheric science, among others, are well developed.

Raman spectroscopy of static gases started very soon after the discovery of the Raman effect in 1928. The development of lasers in the 60's as ideal exciting sources for Raman scattering, and of the charge-coupled detectors (CCD) and computer-assisted spectrometers in the 90's have been the major steps towards

present day maturity. Good quality Raman spectra of flowing rarefied gases can be recorded today under almost-routine conditions. Between the 60's and the 90's the non-linear Raman techniques contributed with additional possibilities to the research of gas media, also under dynamical conditions [4-6].

In the present scope, the relevant merits of Raman spectroscopy are: 1) Universality, since all molecular species are Raman-detectable; 2) Non-intrusivity, probing the flow field with space resolution of few μm ; 3) Number density sensitivity down to 10^{20} m^{-3} under routine conditions; 4) Stability for periods of several hours; 5) Thermal range from sub-kelvin to kilo-kelvin. These capabilities prove ideal for quantitative investigation in rarefied gas dynamics when combined with *ad-hoc* devised expansion chambers.

It must be stressed, however, that Raman spectroscopy in supersonic jets differs very much from the usual molecular beam methods, where only terminal properties can be measured. In contrast, in Raman-jet experiments most part of the 3D flow field is experimentally accessible, from very close to the nozzle ($\approx 50 \mu\text{m}$), up to almost terminal conditions.

Quantitative Raman spectroscopy of rarefied flows requires some sort of dedicated facility whose main elements are: 1) Raman spectrometer ($\approx 1 \text{ m}$ focal length) equipped with liquid- N_2 cooled CCD detector; 2) PC and software for control of spectrometer and CCD detector, and for management of spectra; 3) *cw*-laser of $\approx 5 \text{ W}$ in the visible; 4) Gas expansion chamber; 5) High capacity vacuum line; 6) Gas feeding line with pressure regulators and mass-flow controllers; 7) Nozzle; 8) Optical elements for excitation and collection of Raman scattering; 9) Motorized stages for nozzle XYZ-positioning and optical alignment inside of expansion chamber, 10) High accuracy pressure gauges and mass-flow controllers.

The parts listed above are based on standard material, with exception of the gas expansion chamber and the nozzles. The assembly of all these parts in a vibration-free system imposed by the spectroscopic stability, requires some additional robust structures (not commercial). Two such diagnostic facilities are operative at the Laboratory of Molecular Fluid Dynamics (CSIC, Madrid). They are based on aluminum box-like expansion chambers of internal volumen $\approx 0.16 \text{ m}^3$. Nozzles are either orifice-type or slit-type, producing 2D and 3D steady free-jet flows, respectively. The nozzles, of exit areas between 50 to 400000 μm^2 , operate at stagnation pressures between 16 and 0.03 bars. One of the diagnostic facilities is supplied with a cryogenic nozzle (not commercial) operating at stagnation temperatures down to 25 K.

FIGURE 1. Raman jet set up: excitation-collection.

FIGURE 2. LMFD-Raman jet diagnostics facility (top view).

Raman scattering excitation/collection set-up is shown in Fig 1. Figure 2 shows a scheme of one of the facilities. Detail of the jet and of the scattering region (inset) is shown in Fig. 3. The dashed area in the inset of Fig. 3 is the region seen by the CCD detector of the spectrometer, which determines the spatial resolution of the experiment. Points to be probed in a $12 \times 12 \times 50 \text{ mm}^3$ flow field are selected by XYZ-displacing of the nozzle with step-size resolution of $0.1 \mu\text{m}$.

The quantities directly measured at any accessible point of the flow field are number density (n), and the populations (P_J) of the rotational levels J , regardless of whether the point measured is in local Maxwell-Boltzmann equilibrium or not; n and P_J are measured from the Raman intensities, either from vibrational Q-branches, or from the rotational spectrum [7,8]. Vibrational populations (P_v) can also be measured for levels with sufficient population. The usual dynamical ranges are $10^{20} \leq n \leq 10^{26} \text{ m}^{-3}$ and $4 \leq T \leq 250 \text{ K}$

for nozzles at room temperature. Temperatures down to 0.1 K can be attained with cryogenic nozzles [9].

FIGURE 3. Raman jet excitation (detail).

Measured number densities are accurate to $\approx 1\%$ at $n \approx 10^{24} \text{ m}^{-3}$, and $\approx 10\%$ at $n \approx 10^{20} \text{ m}^{-3}$. Rotational populations are accurate to $\approx 0.1\%$ in optimal cases. In isentropic regions of the flow field (e.g. zone of silence) the translational temperature can be inferred from the former data assuming entropy invariance, while flow velocities are inferred by conservation of energy along the jet [10-12].

A number of problems in rarefied gas dynamics studied so far in the facilities described above are presented next. The first one is the mapping and features of the jet, which serves as a visual guide to the other problems discussed (always keeping in mind the Boltzmann equation and its collision integral as a target).

JET MAPPING AND FEATURES

Density and thermal maps of steady free jets by Raman spectroscopy [13] are shown in Figs. 4 and 5. These maps were synthesized from 2200 Raman spectra (per map) recorded in a grid of points overlapping the flow field. Identified and quantified features are: zone of silence, barrel shock, normal shock, interference between shocks, thermal overshoot, rethermalized wake, and wake cold channels. All these features have been interpreted by numerical simulation in the quasi-gas-dynamic approach [13,14].

FIGURE 4. Raman map of a supersonic jet: Density.

FIGURE 5. Raman map of a supersonic jet: Rotational temperature.

Other examples from supersonic jets quantitatively investigated by Raman spectroscopy are shown in Figs. 6-16: On-axis mass enrichment in mixed $\text{H}_2 + \text{N}_2$ jets is shown in Fig. 6; the permeation of the barrel and normal shocks by a residual gas (H_2) external to a jet of N_2 is shown in Figs. 7 and 8; the breakdown of rotational-translational equilibrium in a H_2 jet is shown in Fig 9. Many other related problems can be studied by Raman diagnostics under comparable level of detail.

FIGURE 6. Heavy species on-axis enrichment.

FIGURE 7. Background H₂ through N₂ barrel.

FIGURE 8. Background H₂ through N₂ shock.

SHOCK WAVES

Mott-Smith's (MS) model [15], which is based on solving Boltzmann equation, offers a first approximation to the shock wave problem. Experimental proof in favour of the two-temperature distribution function predicted by the MS-model was given for a He normal shock [16]. The power of Raman diagnostics for such studies is shown in Fig. 10, where the evolution of rotational Raman spectra recorded across a $M = 10.6$ shock wave of N₂ is presented. The nine spectra shown were recorded within 0.5 mm. The first one (top) shows a rotational temperature of 14 K corresponding to the cold molecules prior to the onset of the shock, while the last one (bottom), at 265 K, is due to the rethermalized molecules at the end of the shock. The intermediate spectra do not obey Boltzmann distribution. They can be interpreted in terms of the progressive mixing of cold and rethermalized molecules inside the shock, in full agreement with MS-model [8,15]. A molecular interpretation based on the master equation discussed below is under way.

FIGURE 9. Breakdown of thermal equilibrium in H₂ jet.

FIGURE 10. Raman spectra across N₂ shock.

BOLTZMANN EQUATION AND COLLISION INTEGRAL

Straightforward experiments on Boltzmann collision integral are possible in the zone of silence of a supersonic jet, specially in its paraxial region. Since the information gained from Raman spectroscopy is of quantum nature, it can be employed on the generalized Boltzmann equation [1-3]

$$\partial f_i / \partial t + \mathbf{v} \cdot \nabla f_i = (\delta f_i / \delta t)_{coll}, \quad (1)$$

where $f_i(\mathbf{r}, \mathbf{v}, t)$ is the distribution function of velocity $\mathbf{v}$ for molecules in quantum state i at the position $\mathbf{r}$ and time instant t . The left-hand term (LHT) in Eq. (1) accounts for the changes in f_i due to geometrical

effects along the time between collisions, while the right-hand term is the so called Boltzmann collision integral (BCI). It refers to the changes of f_i due to the collisions. Its explicit form reads [2]

$$\left(\frac{\delta f_i(\mathbf{r}, \mathbf{v}_1, t)}{\delta t}\right)_{coll} = \sum_{jlm} \int \int \int \left[f_\ell(\mathbf{r}, \mathbf{v}_2', t) f_m(\mathbf{r}, \mathbf{v}_1', t) \frac{(2i+1)(2j+1)}{(2\ell+1)(2m+1)} - f_j(\mathbf{r}, \mathbf{v}_2, t) f_i(\mathbf{r}, \mathbf{v}_1, t) \right] \times |\mathbf{v}_1 - \mathbf{v}_2| \sigma_{ij \rightarrow \ell m} dv_{2,x} dv_{2,y} dv_{2,z}, \quad (2)$$

where $\mathbf{v}_1$, $\mathbf{v}_2$ and $\mathbf{v}_1'$, $\mathbf{v}_2'$ are, respectively, the precollisional and postcollisional velocities of collisional partners 1 and 2. In turn i, j and ℓ, m are respectively the precollisional and postcollisional rotational quantum numbers of the collision partners; $\sigma_{ij \rightarrow \ell m}$ is the space averaged cross section for the $ij \rightarrow \ell m$ collisional event at the kinetic energy $E = \mu|\mathbf{v}_2 - \mathbf{v}_1|^2/2$, where μ is the reduced mass of partners 1 and 2.

The microscopic form (2) provides the basis for the macroscopic gas dynamic equations, and for the molecular transport coefficients appearing in them, like thermal conductivity, shear and bulk viscosities, and diffusion coefficient, which have been formulated in terms of the collision cross sections $\sigma_{ij \rightarrow \ell m}$ [1,3,17].

The molecular approach described above suffers from severe limitations, namely a) Transport coefficients derived through Chapman-Enskog expansion are valid only at quasi-equilibrium between translation and internal degrees of freedom. b) Reliable state-to-state cross sections $\sigma_{ij \rightarrow \ell m}$ are available to date just for H_2 (10-300 K), and N_2 (4-50 K) [12,18]. c) the $\sigma_{ij \rightarrow \ell m}$'s are so sensitive to the anisotropy of the intermolecular potential that simplified models lead to uncertain results. d) For molecules other than H_2 the number of $\sigma_{ij \rightarrow \ell m}$'s required at $T \geq 300$ K is that large that the computational effort to calculate them is prohibitive at present. Furthermore, this number increases rapidly with temperature.

Such demanding conditions for an accurate knowledge of the core of BCI (2), which is the set of $\sigma_{ij \rightarrow \ell m}$'s, has impaired up to now the full exploitation of Boltzmann equation. However, recent experimental/computational work [12,18,19] has shown that Eqs. (1) and (2) are open to direct experimental investigation at the zone of silence of steady supersonic free jets. Such region, which is accepted to be adiabatic and isentropic, is easily accessible in the laboratory for a wide range of conditions observable by Raman spectroscopy.

A peculiarity of the zone of silence is the intrinsic breakdown of equilibrium between translational and internal degrees of freedom. Below 300 K, vibrational degrees of freedom tend to become frozen in light molecules (H_2 , H_2O , N_2 , O_2), while rotation is subject to a more or less marked collisional interchange of energy with translation. Well-defined rotational and translational temperatures, T_r and T_t , have been shown experimentally for various stagnation conditions [18,20,21], with $T_r - T_t$ differences increasing with distance to the nozzle, up to the normal shock. This suggests that the one-particle distribution function can be factorized to a good approximation as $f_i = n P_i Q$, where $n(\mathbf{r}, t)$ is the instantaneous number density at position $\mathbf{r}$, $P_i(\mathbf{r}, t)$ is the instantaneous population of internal state i , and Q is the Maxwellian velocity distribution at the local translational temperature T_t in a jet with local flow velocity $\mathbf{v}_0(\mathbf{r})$. In turn, the internal populations obey a distribution of the form $P_i = g_i \exp(-E_i/kT_{int})/Z_{int}(T_{int})$, where E_i is the energy of the internal state i , g_i its degeneracy, and Z_{int} the internal state partition function at the temperature T_{int} . Under these approximation the set of gas-dynamic conservation equations governing the paraxial region of the zone of silence of supersonic jets reduces to [19]

$$(D/Dt)P_i + P_i \nabla \cdot \mathbf{v}_0 = (\delta P_i / \delta t)_{coll}, \quad (\text{matter}) \quad (3)$$

$$\Delta S = 0, \quad (\text{entropy}) \quad (4)$$

$$\Delta(H + |\mathbf{v}_0|^2/2) = 0. \quad (\text{energy}) \quad (5)$$

In Eq. (3) $D/Dt = \partial/\partial t + \mathbf{v}_0 \cdot \nabla$ stands for the substantial derivative operator, while the right-hand-term accounts for the changes of internal population P_i along time due to collisions.

A first experimental difficulty with the collision integral (2) arises from the $\sigma_{ij \rightarrow \ell m}$'s, which are functions of the kinetic collision energy E , a quantity not easily amenable to direct spectroscopic observation in regions close to the nozzle. This difficulty is overcome by transforming the domain of energies to the domain of (kinetic) temperatures T_t by means of the collision rate coefficients

$$k_{ij \rightarrow \ell m}(T_t) = \frac{\langle v \rangle}{(k_B T_t)^2} \int_{E_s}^{\infty} \frac{\sigma_{ij \rightarrow \ell m}(E)}{\exp(E/k_B T_t)} E dE, \quad (6)$$

where $\langle v \rangle = (8k_B T_t / \pi \mu)^{1/2}$ is the mean relative velocity of the colliding partners of reduced mass μ , and E_s is the minimum kinetic energy for the internal states m and ℓ 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, ℓ, m may be identified with the rotational quantum numbers. Taking into account (6), and the detailed balance for up and down collisional processes consubstantial to $f_i = n P_i Q$, Boltzmann equation (1) for the paraxial region of a stationary supersonic jet leads to the non-linear master equation (MEQ) [22]

$$v_0(z) \frac{dP_i}{dz} = n(z) \sum_{j\ell m} (-P_i(z) P_j(z) k_{ij \rightarrow \ell m} + P_\ell(z) P_m(z) k_{\ell m \rightarrow ij}). \quad (7)$$

This non-linear 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 by Raman spectroscopy, while the translational temperature T_t implicit in the k 's, and the flow velocity v_0 , can also be inferred from the Raman data by means of Eqs. (4) and (5) respectively. This way MEQ (7) can be treated as a linear algebraic equation where the $k_{ij \rightarrow \ell m}$ rate coefficients are the unknowns. These may be supplied by high level scattering codes [23,24] using suited intermolecular potentials, and can be assessed experimentally by means of MEQ (7). In favourable cases, the rates may be derived inverting the MEQ (7). Both options have been explored recently, showing that the collisional problem is fully tractable at temperatures below 300 K for H_2 jets [11,12,19]. In this range all relevant $k_{ij \rightarrow \ell m}$ rates for $H_2:H_2$ inelastic collisions have been evaluated at the highest level of collisional scattering theory, showing full consistency with Boltzmann equation in the form of the MEQ (7) when completed with the Raman experimental data from the paraxial region of the jet. The agreement with the old, but accurate data on acoustic relaxation time [25,26] proved excellent.

In the simplest molecule:molecule collisional problem ($H_2:H_2$) just eleven $k_{ij \rightarrow \ell m}$ rates are relevant at $T_t \leq 300$. An estimate of the collisional complexity may be inferred from Fig. 11, which displays the collisional spectrum at the point $z = 100 \mu m$ downstream in the H_2 jet where $T_t = 120$ K and $T_r = 198$ K. This collisional spectrum shows the different elementary collisional processes participating in populating and depleting the $J = 0$ rotational level, and the absolute contribution to the global $T_r \neq T_t$ non-equilibrium of the medium. Note in Fig. 11 the relevance of the $30 \rightarrow 12$ process deexciting one of the colliding molecules while the partner molecule becomes excited. This mixed down-up processes are hard to account for in classical as well as in simplified quantum models.

FIGURE 11. Collisional spectrum for $J = 0$ rotational level in supersonic jet of nH_2 at $z/D = 0.3$.

FIGURE 12. Selected rate coefficients for $H_2:H_2$ and $N_2:N_2$ inelastic collisions.

The collisional problem of heavier molecules like N_2 is far more involved. A recent study employing MEQ (7) complemented by Raman data from the jet [18], shows that at $T_t = 10$ K the number of relevant collisional channels is about 50. This is the number of inelastic $\sigma_{ij \rightarrow \ell m}$ cross sections in Boltzmann collision integral (2) at 10 K. This figure rises to ≈ 250 at 40 K, to about thousand at 77 K, and to several thousand at 300 K. Combining computation and experiment, reliable sets of N_2 cross-sections and rates have already been obtained for $T_t \leq 40$ K. Extending these results to $T_t = 300$ K is a formidable computational and experimental task. However, the fast development of parallel computer codes for the collisional scattering problem, and some instrumental improvements might reduce the BCI problem to affordable

limits in few years. Selected homologous rates for $\text{H}_2:\text{H}_2$ and $\text{N}_2:\text{N}_2$ inelastic collisions are shown in Fig. 12 for comparison.

RELAXATION

The thermal non-equilibrium $T_{int} \neq T_t$ between the internal and translational degrees of freedom is a marked feature of supersonic jets and rarefied gas media. This phenomenon has often been interpreted in the frame of the so-called relaxation equation [20, and cites therein]

$$dT_{int}/dt = -(T_{int} - T_t)/\tau, \quad (8)$$

where τ is a "relaxation time". Equation (8) has been criticized [22,27] because of its phenomenological character and lack of solid physical background. However, it can be derived straight from Boltzmann equation (1) and collision integral (2), after transformation into MEQ (7). For instance, for the rotational case, employing the detailed balance and the approximation $T_r \approx \beta B \sum_i i(i+1)P_i$, and adding in (7) over the rotational levels i , one obtains the relaxation equation

$$dT_r/dt = -(n\beta B/4) \sum_{ij\ell m} A_{ij\ell m} (1 - e^{X A_{ij \rightarrow \ell m}}) P_\ell P_m k_{\ell m \rightarrow ij}, \quad (9)$$

where $\beta = 1.4388 \text{ cm K}$, B is the rotational constant in cm^{-1} , $X = \beta B(T_t^{-1} - T_r^{-1})$ is the equilibrium breakdown quantifier, and $A_{ij\ell m} = \ell(\ell+1) + m(m+1) - i(i+1) - j(j+1)$.

Power expansion of the exponential term in (9) leads to the series

$$dT_r/dt = -(T_r - T_t)a_1 + (T_r - T_t)^2 a_2 - (T_r - T_t)^3 a_3 + \dots, \quad (10)$$

with coefficients

$$a_s = \frac{n(\beta B)^{s+1}}{s!4(T_r T_t)^s} \sum_{ij\ell m} (A_{ij \rightarrow \ell m})^{s+1} k_{\ell m \rightarrow ij} P_\ell P_m. \quad (11)$$

Truncation of (10) in the first term leads to the well-known relaxation equation (8) for the rotational case, with relaxation time $\tau = 1/a_1$. However, the convergence of (10) is very slow and such truncation leads to severe errors if T_r and T_t differ by more than $\approx 10\%$, a limit for the validity of the relaxation equation (8). For N_2 supersonic jets this limit is attained within the first 30 nozzle diameters, being in general Eq. (8) invalid for terminal conditions, as has often been employed in the literature.

Since the rotational cross section is related with the relaxation time by $\sigma_r = 1/(\tau n \langle v_{coll} \rangle)$, one obtains

$$\sigma_r = \frac{1}{4\langle v_{coll} \rangle} \frac{(\beta B)^2}{T_r T_t} \sum_{ij\ell m} P_\ell P_m (A_{ij \rightarrow \ell m})^2 k_{\ell m \rightarrow ij}, \quad (12)$$

for the molecular form, which is valid for moderate $T_r \neq T_t$ breakdown. The bulk viscosity of the gas η_V is a simple function of τ , or σ_r [28] and can also be expressed in molecular terms by means of (12).

A number of supersonic jets of N_2 investigated recently by Raman spectroscopy [18] have provide the data for Eq. (12) in the range $4 \leq T_t \leq 40 \text{ K}$. The corresponding cross section σ_r is shown in Fig. 13 jointly with the results for $T_t > 77 \text{ K}$ derived from acoustic experiments [28]. Although Raman jet and acoustic experiments differ very much in nature, the σ_r values derived from them connect smoothly through the link provided by Boltzmann collision integral (2).

CONDENSATION

The zone of silence of supersonic jets is a suitable physical environment for the study of condensation from the onset by means of Raman spectroscopy [9,29,30]. Due to its high spatial resolution in the jet, quantitative information is obtained at the very same spot and time instant where condensation is occurring, with simultaneous characterization of the local density and temperature conditions. Although less sensitive than the methods based on ionization and terminal detection of the fragments, Raman spectroscopy is non-intrusive and provides a sound information, overcoming the problem of evaporation, fragmentation,

and recombination processes occurring up to the far away located detector. Preliminary quantitative studies of cluster growth have been performed on CO₂ jets by means of Raman/Rayleigh diagnostics [29]. The (CO₂)_N cluster mean size evolution along the expansion is shown in Fig. 14 as a function of stagnation pressure.

FIGURE 13. Rotational relaxation cross section of N₂.

FIGURE 14. Size of in-jet formed (CO₂)_N clusters by Raman/Rayleigh diagnostics.

Since the flow is laminar in the zone of silence, with well-defined flow velocity, the high spatial resolution of Raman diagnostics enables a time resolution in the domain of nanoseconds, as shown in Fig. 15 for the condensation of para-H₂ [9]. Figure 15 shows the formation and evolution of size-resolved para-H₂ clusters by means of a cryogenic nozzle at 25 K, which allows reaching sub-kelvin temperatures in the jet. This opens appealing possibilities for the study of nucleation and presumed superfluidity of para-H₂. In this line of research, the fundamental processes of homogeneous nucleation, which are the three-body formation (*f*) and destruction (*d*) of para-H₂ dimers

have been studied recently in detail [30]. The kinetic equations employed in this study for the evolution of monomer and dimer mole fractions, X_1 and X_2 , along the jet are the three-body variants of MEQ (7),

$$v_0(z) dX_1/dz = n^2(z)(-2k_f X_1^3 - k_d X_1^2 X_2/2), \quad (15)$$

$$v_0(z) dX_2/dz = n^2(z)(2k_f X_1^3 - k_d X_1^2 X_2), \quad (16)$$

which suggest the possibility of considering Boltzmann collision integral (2) at a higher level of complexity for the study of the first steps of homogeneous molecular nucleation. The three-body dimer formation and destruction rate coefficients, k_f and k_d , in pure pH₂ cryogenic jets are shown in Fig. 16.

FINAL COMMENTS

The examples discussed above were aimed at exploring the instrumental possibilities of Raman spectroscopy for the quantitative study of rarefied gas dynamic problems, providing a wealth of reference experimental data for numerical tests in computational fluid dynamics. Many other problems like the interference between the flow fields of twin nozzles, the behavior of counterpropagating jets, or the characterization of shocks in front, or around bodies of different shapes under different conditions of rarefaction, or the detachment of boundary layers, can be studied with similar, or with *ad-hoc* adapted facilities. Since one of the advantages of Raman spectroscopy is its superb spatial resolution, the use of specific nozzles and expansion chambers may provide the basis for miniature hypersonic wind tunnels of low operation cost.

From the methodological point of view, Boltzmann collision integral, transformed from the domain of energies into the domain of temperatures, and supported with high accuracy Raman data from the zone of silence of supersonic jets, permit us to unify the study of inelastic collisions, relaxation, and homogeneous nucleation within a common theoretical frame. Practical applications to the realm of approximations-free transport coefficients, as well as to condensation kinetics are still utopic. However, the methodology is well established, and the progress is a question of computational power, and of cooperation between quantum chemists, experimentalists, and fluid dynamics experts. Accurate intermolecular potentials appear to date as a bottleneck [19], which can be overcome in part by the present methodology.

FIGURE 15. Small $(\text{pH}_2)_N$ clusters formed in jet.

FIGURE 16. Three-body formation and destruction rates of pH_2 dimer.

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REFERENCES

1. C. S. Wang-Chang and G. E. Uhlenbeck, Univ. Michigan Rept. CM-681 (1951).
2. L. Waldmann, in *Handbuch der Physik*. Vol XII, p. 452, edited by S. Flügge, Berlin, Springer (1958).
3. C. S. Wang-Chang, G. E. Uhlenbeck, and J. deBoer, *Studies in Statistical Mechanics*, Vol. 2., edited by J. deBoer and G. E. Uhlenbeck, Amsterdam, North Holland (1964).
4. P. Huber-Wälchli and J. W. Nibler, *J. Chem. Phys.* **76**, 273 (1982).
5. J. W. Nibler and J. J. Yang, *Ann. Rev. Phys. Chem.* **38**, 349 (1987).
6. I. Ribet, B. Scherrer, P. Bourchardy, P. Pot, J. P. Taran, et al., *J. Raman Spectrosc.*, **31**, 689 (2000).
7. G. Tejeda, B. Maté, J. M. Fernández-Sánchez, and S. Montero, *Phys. Rev. Lett.* **76**, 34 (1996).
8. A. Ramos, B. Maté, G. Tejeda, J. M. Fernández, and S. Montero, *Phys. Rev. E*, **62**, 4940 (2000).
9. G. Tejeda, J. M. Fernández, S. Montero, D. Blume, et al., *Phys. Rev. Lett.* **92**, 223401 (2004).
10. B. Maté, F. Thibault, A. Ramos, G. Tejeda, J. M. Fernández, et al., *J. Chem. Phys.* **118**, 4477 (2003).
11. B. Maté, F. Thibault, G. Tejeda, J. M. Fernández, and S. Montero, *J. Chem. Phys.* **122**, 064313 (2005).
12. S. Montero, F. Thibault, G. Tejeda, and J. M. Fernández, *J. Chem. Phys.* **125**, 124301 (2006).
13. B. Maté, I. A. Graur, T. Elizarova, I. Chirokov, G. Tejeda, et al., *J. Fluid Mech.* **426**, 177 (2001).
14. I. A. Graur, T. G. Elizarova, A. Ramos, G. Tejeda, et al., *J. Fluid Mech.* **504**, 239 (2004).
15. H. M. Mott-Smith, *Phys. Rev.*, **82**, 885 (1951).
16. G. Pham-Van-Diep, D. Erwin, and E. P. Muntz, *Science* **245**, 624 (1989).
17. V. M. Zhdanov, *Transport Processes in Multicomponent Plasma*, Taylor & Francis, London (2002).
18. J. P. Fonfría, G. Tejeda, F. Thibault, J. M. Fernández, et al., *J. Chem. Phys.* **127**, 134305 (2007).
19. G. Tejeda, F. Thibault, J. M. Fernández, and S. Montero, *J. Chem. Phys.*, **128**, 224308 (2008).
20. F. J. Aoiz, T. Díez-Rojo, V. J. Herrero, B. Martínez-Haya, et al., *J. Phys. Chem. A*, **103**, 823 (1999).
21. A. Ramos, G. Tejeda, J. M. Fernández, and S. Montero, *Phys. Rev. A*, **66**, 022702 (2002).
22. H. Rabitz and S. Lam, *J. Chem. Phys.* **63**, 3532 (1975).
23. J. M. Hutson and S. Green, MOLSCAT-14, Collab. Comput. Proj. n°6 of the UK SERC, 1994.
24. D. R. Flower, G. Bourhis, and J. -M. Launay, *Comput. Phys. Commun.* **131**, 187 (2000).
25. R. M. Jonkman, G. J. Prangasma, I. Ertas, H. F. P. Knaap, et al., *Physica* **38**, 441 (1968).
26. G. J. Prangasma, L. J. M. Borsboom, H. F. P. Knaap, et al., *Physica* **61**, 527 (1972).
27. L. K. Randeniya and M. A. Smith, *J. Chem. Phys.*, **93**, 663 (1990).
28. G. J. Prangasma, A. H. Alberga, and J. J. M. Beenakker, *Physica*, **64**, 278 (1973).
29. A. Ramos, J. M. Fernández, G. Tejeda, and S. Montero, *Phys. Rev. A*, **72**, 053204 (2005).
30. J. H. Morilla, J. M. Fernández, G. Tejeda, and S. Montero, (in preparation).