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Direct evidences of scattering resonances enhancement in the vibrational relaxation of $I^2(B^3\Pi^+_{0u}, v' = 21)$ by collisions with He at very low temperatures

Iván Cabanillas-Vidosa, Gustavo A. Pino, Carlos A. Rinaldi, Juan C. Ferrero *

Centro Láser de Ciencias Moleculares, INFIQC, Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba Pabellón Argentina, Ciudad Universitaria, 5000 Córdoba, Argentina

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Abstract

The vibrational deactivation of $I_2(B, v' = 21)$ by He in the low energy regime, was studied under single collision conditions, in a supersonic expansion. The time resolved fluorescence signal (TRFS) from the $(B; v' = 21) \rightarrow (X; v'' = 1)$ transition was collected at several distances from the nozzle to access different local temperatures in the range (0.17–6) K. From the analysis of the TRFS the value of the relaxation cross-section was extracted and it showed to decrease with energy through a series of peaks. This experimental observation, confirms the role of scattering (mainly orbiting) resonances as theoretically postulated previously.

1. Introduction

Over the past two decades, experiments have been performed in several laboratories to study the vibrational relaxation of molecules in supersonic jets, which provided information on the relaxation rates of vibrationally excited molecules as a function of the local temperature, by monitoring these processes as a function of the distance from the nozzle.

The $He + I_2$ system has received extra attention in these studies because of the large cross section for vibrational relaxation of $I_2(B, v')$ at very low collision energies [1–9].

Several explanations have been proposed for this unexpected phenomenon, such as the contribution of scattering resonances at kinetic energies near zero [1–5,7,8]. In this regard, several calculations have shown that the occurrence of orbiting resonances or formation of metastable complexes is very likely in that regime and it should increase the collision duration [4,5,8]. Consequently, a longer collision becomes more effective in relaxing the vibrational energy, which is consistent with the notion of van der Waals (vdW) resonances role, earlier suggested by Beswick and coworkers [10].

Another possible explanation for this phenomenon is that at very low energies the vibrational relaxation cross section may achieve reasonably large values even in absence of resonances, as a natural consequence of microscopic reversibility and according to quantum scattering theory [6].

It has been also suggested that the increased opportunities for I_2–He encounters at low collision energies, facilitated by the attractive part of the interaction potential, are sufficient to explain the increment of the vibrational relaxation rate as the temperature drops from 12 to 2 K [9]. This means that the mechanism of vibrational relaxation remains unchanged in the temperature range studied and that the apparent increase in vibrational relaxation efficiency, when scaled with respect to a hard sphere collision rate, is simply a failure of the hard sphere potential at low collision energies to accommodate the full range of collision trajectories.

In the lack of conclusive experimental evidences, the present general consensus is that even though resonances

* Corresponding author.
E-mail address: jferrero@fcq.unc.edu.ar (J.C. Ferrero).

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are not required to explain the results, both mechanisms contribute to some extent to the relaxation process at low collision energies as pointed out by Loomis and co-workers [11] and Gray and Rice [8].

In this respect the experimental results reported in this letter show that the relaxation cross-section is not a monotonical function of energy but shows peaks whose width increases with it, suggesting the presence of scattering resonances that therefore need to be considered at collision energies below 5 cm^{-1}.

2. Experimental

A free jet of I_2 seeded in He was generated by expanding a mixture of 760 Torr of He and the room temperature vapour pressure of I_2 through a 500 μm diameter (d) pulsed nozzle (Solenoid General Valve, Serie 9) into a vacuum chamber kept at a background pressure in the range 5×10^{-7}–8×10^{-6} Torr under operative conditions. The ratio of partial pressure of I_2 to He in the stagnation region was always lower than 0.001 to ensure that only I_2–He collisions were responsible of the I_2 vibrational relaxation.

The second harmonic of a Spectra–Physics (Indi-HG) Nd:YAG laser was used to pump a Lumonics (HD500) dye laser operating with Rh575, tuned to the $(B;v'=21\leftarrow X;v''=0)$ transition of I_2 and focused with a lens ($f=200$ mm) into the centre of the jet. Under this focussing condition, the excited volume was approximately 0.06 mm^3. The distance (x) between the nozzle and the excitation region was varied by moving the valve, mounted on a rail externally controlled, in 1.0 mm steps, from 4.0 to 20.0 mm, to explore different collision energies regions. The minimum distance (4.0 mm) was chosen to ensure single collision conditions during the fluorescence decay of $I_2(B)$. The maximum distance used (20.0 mm) corresponds to a near collision free regime.

Fluorescence from excited I_2 was collected collinear with the jet axis by two lenses ($f_o=150$ mm and $f_i=100$ mm) that render a magnification factor equal to 0.67 and imaged onto the entrance slit of a 30 cm focal length monochromator (McPherson).

It is well known that the main velocity component of the molecules in the jet is along its axis and under the present experimental conditions a maximum velocity of 800 m/s was estimated [12].

Since our detection system is located in front of the jet, the excited molecules that escape from the excitation region, travelling along the jet axis, will be always detected. However if molecules travel with a different angle, they can be lost before they fluoresce and this will affect the determination of the rate constant. In order to evaluate this effect a few experiments were performed collecting the fluorescence at 135° with respect to the jet axis. The rate constants determined with this set-up were exactly the same within to the experimental error that those determined with the collection optics in front of the jet.

Even in the highly improbable case that the whole velocity component (800 m/s) were perpendicular to the jet axis, geometric calculations showed that the fluorescence from all the diffusing molecule should be detected during the fluorescence lifetime (0.8 μs), with the present experimental set-up.

In this respect, the value of the measured rate constant changed only 10% when the aperture of the entrance slits was varied from 0.5 to 1.6 mm, with the collection optics in front of the jet axis. Therefore, most of the experiments were performed with an entrance slit equal to 1.2 mm.

The time resolved fluorescence signal (TRFS) from the $(B;v'=21\rightarrow X;v''=1)$ transition was recorded at the exit slit of the monochromator by a photomultiplier tube (Hamamatsu R636), digitised by a Tektronik (TDS-3034B) oscilloscope and averaged over 512 laser shots and finally fitted in a computer.

3. Results and analysis

Extensive experimental and theoretical investigations have been undertaken to characterize the properties of atoms and molecules within isentropic expansions [13]. The thermodynamics for a perfect gas requires the local temperature (T), pressure (P) and density (ρ), within the expansion region to be related by

$$\frac{T}{T_0}=\left(\frac{P}{P_0}\right)^{\frac{\gamma}{\gamma-1}}=\left(\frac{\rho}{\rho_0}\right)^{\gamma-1}=\left(1+\frac{\gamma-1}{2}M^2\right)^{-1} \quad (1)$$

In this equation T_0, P_0 and ρ_0 represent the temperature, pressure and density of the reservoir gas behind the nozzle, and γ is the heat capacity ratio (C_p/C_v), equal to 5/3 for He and M is the Much number, which is related to the downstream distance in nozzle diameters (x/d) by

$$M=\left(\frac{x}{d}\right)^{(\gamma-1)}\left[C_1+\frac{C_2}{\left(\frac{x}{d}\right)}+\frac{C_3}{\left(\frac{x}{d}\right)^2}+\frac{C_4}{\left(\frac{x}{d}\right)^3}\right]\ \text{for}\ \left(\frac{x}{d}\right)>0.5 \quad (2)$$

where the values of C_1, C_2, C_3, and C_4 where taken from Ref. [13].

Table 1 shows the values of T, calculated from Eqs. (1) and (2), for the conditions of the present experiments, at each reduced distance (x/d), together with the mean collisional energy calculated as $\langle E_k\rangle=3RT/2$. The velocity slip between He and I_2 was neglected since it has been previously shown that under our experimental conditions it only represents less than 10% of the ideal translational temperature [9].

As mentioned previously, the TRFS of the $(B;v'=21\rightarrow X;v''=1)$ I_2 transition was monitored as a function of the collision energy (distance from the nozzle) upon excitation of the $(B;v'=21)$ state. All the signals recorded could be satisfactorily fitted to a single exponential decay with a global decay rate, Γ. Fig. 1 shows a typical TRFS together with the best fit obtained.

The vibrational relaxation rate constant k_v, can be extracted from Γ if the contribution of all the processes