# Elastic Collision Kernels: Theoretical Determination and Direct Observation by Use of Time-Resolved Saturation Spectroscopy in Metastable Neon

Michel Gorlicki, Christian Lerminiaux, and Michel Dumont
*Laboratoire de Physique des Lasers, Laboratoire No. 282 associé au Centre National de la Récherche Scientifique, Université Paris-Nord, F-93430 Villetaneuse, France*

(Received 27 July 1982)

Collision kernels describing elastic collision effects in saturation spectroscopy are completely calculated for the metastable $^3P_0$ state of neon, starting from true experiment-deduced potentials. Collision processes with and without metastability exchange are respectively considered. A direct observation of these two kernels is provided by a two-laser time-resolved saturated absorption experiment. They are in good agreement with theory.

PACS numbers: 34.40.+n, 32.70.Jz

Line shapes in saturation spectroscopy are strongly affected by collisions. As in linear spectroscopy they are sensitive to quenching collisions and to dephasing collisions (broadening and shift), but in addition, as was pointed out early on, they are sensitive to velocity changing collisions (VCC). Many theoretical and experimental works have been devoted to this subject.

The quantity of interest is the collision kernel $W(v' \rightarrow v)$ which describes the probability per unit time that a collision will change the projection of the atomic velocity on the laser beam axis from $v'$ to $v$. Many theoretical papers deal with the formal determination of the kernel from scattering amplitudes (sometimes from the interatomic potentials) and with the evaluation of the line shape from the kernel.[1-5] Nevertheless in all detailed calculations of line shapes phenomenological potentials (hard sphere,[3] $R^{-6}$,[5] Lennard-Jones) or phenomenological kernels (Keilson and Störer[6]) are used. In this paper, we present the first attempt to link all the steps from a realistic potential to a direct experimental observation of the kernel. The metastable $^3P_0$ level of neon ($1s_3$ in Paschen notation) has been considered, since the Ne*-Ne potentials had been calculated and the differential cross sections measured.

Experimentally the situation is comparable: Many experiments have been performed, but they have been interpreted with phenomenological kernels (strong or weak collisions[6]). Furthermore in several cases the observed background (strong collisions) or the broadening of saturation peaks (weak collisions) is actually produced by several collisions for each atom and does not clearly represent the kernel.

In our experiments we used a transient method previously described,[7] which has been improved to allow the recording of the saturation line shape after a very short time delay following the switching on of the saturating beam. Thus, the observed signal is the result of only one collision per atom. Another novel feature of this work lies in the calculation of a metastability exchange kernel and in its experimental observation in a mixture of two isotopes.

Because of its short lifetime, the upper level of the transition ($2p_2$ for the 613.3-nm line or $2p_5$ for the 626.6-nm line) provides a negligible contribution to the saturation signal. On the other hand, when a collision changes the velocity of an atom that is in a coherent superposition of both levels, this coherence is destroyed, since very different interatomic potentials are involved[8] (except for very small scattering angles unresolved in our experiments). Therefore the observed VCC signal is only due to the conservation of the population of the $^3P_0$ metastable level.

The Ne*-Ne potentials for the metastable Ne levels have been calculated *ab initio* by Cohen and Schneider (CS).[9] Differential cross sections have been measured by crossed-beam experiments.[10,11] To explain these experimental results, Colomb de Daunant *et al.* have modified the CS potentials and have calculated, by a Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximation, the scattering amplitudes $f_g$ and $f_u$ (symmetric and antisymmetric), in good agreement with the observed cross sections.[12] We used here the metastability-exchange cross section $\sigma_e = \frac{1}{4}|f_u - f_g|^2$ and the direct one $\sigma_d = \frac{1}{4}|f_u + f_g|^2$ deduced from these calculations. In the case when the colliding atoms are of the same isotopic species, indistinguishability does not allow us to separate the two processes. Nevertheless the correct calculation shows that simply adding the cross sections is a good approximation since the interference terms are small.

The average over velocities in the gas is performed in two steps. In the first one the three-dimensional kernel $W(\vec{v}' \to \vec{v})$ is calculated by averaging over the velocity distribution of the atoms in the ground state. The second step is the average over transverse velocity components of the excited atoms.

Each elementary collision is defined by four velocities $(\vec{v}', \vec{v}_p' \to \vec{v}, \vec{v}_p)$, where the subscript $p$ indicates the atom which was in the ground state before the collision (the perturber). The kernel is obtained by averaging over $\vec{v}_p'$ and $\vec{v}_p$ for the direct process and over $\vec{v}_p'$ and $\vec{v}$ for the exchange one. For exchange Rautian's formula[3] must be replaced by

$$W_e(\vec{v}' \to \vec{v}_p) = 2N_p \int \sigma_e(\theta, E) W(\vec{v}_p') \delta(v_r'^2 - v_r^2) \delta(\vec{v}_{\text{c.m.}}' - \vec{v}_{\text{c.m.}}) d^3v_p' \, d^3v$$

where $\vec{v}_r$ and $\vec{v}_{\text{c.m.}}$ are the relative and center-of-mass velocities. As has been done by Ward, Cooper, and Smith[2] for the direct kernel, this six-dimensional integral can be reduced to a simple integral,

$$W_e(\vec{v}' \to \vec{v}_p) = \frac{2}{\sqrt{\pi}} N_P \frac{(1+R)^2}{R u_p^2} t \int_1^{|1/\alpha|} x\, dx \exp\{-t^2x^2 - (R+1)\vec{V}' \cdot \vec{t}(1 - \alpha x^2) - V'^2\}$$
$$\times I_0\big((R+1)|\vec{V}' \times \vec{t}|(x^2-1)^{1/2}(1-\alpha^2x^2)^{1/2}\big)\sigma_e[\theta(x), E(x)],$$

where $u_p = (2kT/Mp)^{1/2}$; $R = M/M_p$ (mass ratio); $\alpha = (R-1)/(R+1)$; $\mu^{-1} = M^{-1} + M_p^{-1}$; $\vec{t} = (\vec{v}_p - \vec{v}')/u_p$; $\vec{V}' = \vec{v}'/u_p$;

$$\theta(x) = \cos^{-1}\{\tfrac{1}{2}(R+1^2)(2/x^2 - 1 - \alpha^2)\};$$

$E(x) = \frac{1}{2}\mu[tu_px^2]$; and $I_0$ is the modified Bessel function. Among the four integrations over transverse velocities, one is straightforward. The four remaining integrations are computed with a Monte-Carlo method [$\sigma(\theta, E)$ having first been approximated analytically]. The calculated kernels are shown in Fig. 1 for $^{22}$Ne*-$^{20}$Ne collisions with an initial value $v' = u_{22}$. The exchange kernel is very broad (~ thermal width $u_{22}$) but a memory of the initial velocity is evident. The direct kernel presents a very sharp asymmetric peak near the initial velocity with small broad wings. This behavior is characteristic of sharply peaked forward scattering: The average deflection is small and the kernel is narrow, unless the excitation is transferred to the perturber, the final velocity of which is not very different from its initial randomly distributed value.

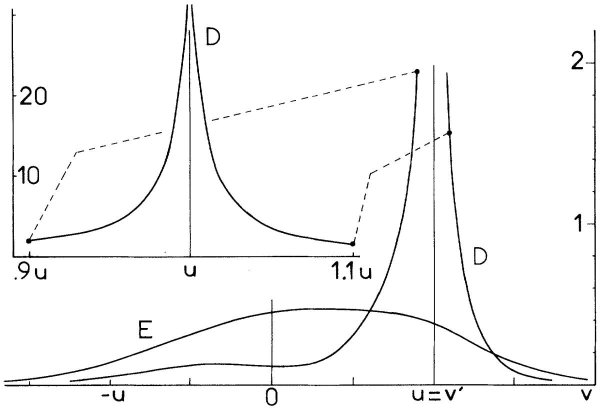

FIG. 1. Calculated direct ($D$) and exchange ($E$) kernels for the initial system $^{22}$Ne*($^3P_0$)-$^{20}$Ne, with $v'$($^{22}$Ne*) = $u_{22}$. The direct-kernel narrow peak corresponds to nearly forward scattering, while the exchange-kernel asymmetry (persistence of initial velocity) and the direct-kernel wings are related to wide-angle regions of scattering amplitudes. Units are arbitrary.

Transient saturated absorption experiments have been described in Ref. 7; they are performed in a low-pressure neon cell (10 to 40 mTorr) excited by an rf discharge. The saturating beam and the probe beam are produced by two independent cw dye lasers stabilized on magnetically tuned saturated absorption signals produced by two auxiliary neon cells.[13] Both beams are shaped in rectangular pulses. A short probe pulse (400 ns) monitors the absorption of the cell with a delay time after the beginning of the saturation pulse (buildup of the saturation) or after the end of this pulse (relaxation). The experiments reported here are

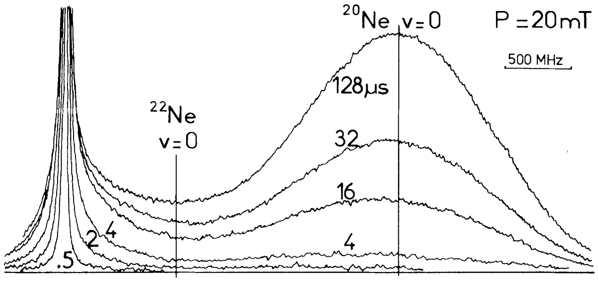

FIG. 2. Time-resolved saturation spectrum for increasing delays, in a 10% $^{22}$Ne–90% $^{20}$Ne mixture (arbitrary units).

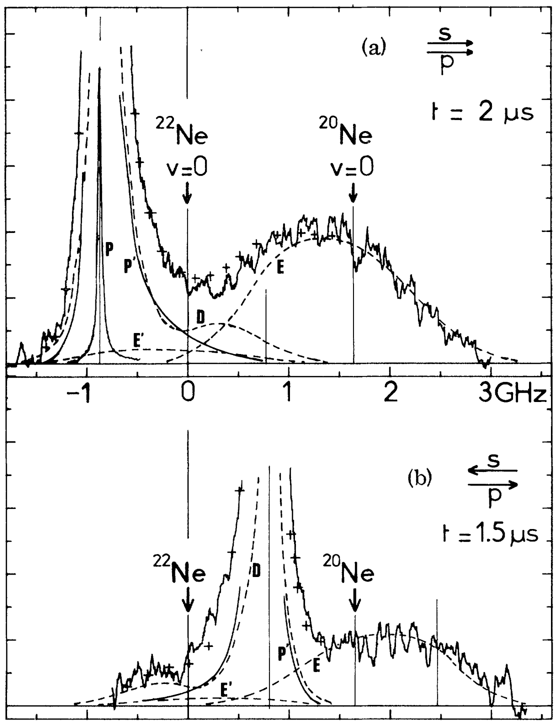

FIG. 3. Recorded line shapes for (a) copropagating and (b) counterpropagating laser beams, giving complementary kernel features. $P$ is the saturation peak, width 40 MHz (sensitivity divided by 50). $P'$ is the calculated wings of the peak (asymmetry due to the Gaussian factor). $D$ is the direct kernel. $E$ and $E'$ are exchange kernels for $^{20}$Ne and $^{22}$Ne, respectively. Crosses are the sum $D+E+E'+F$. The total amplitude is the only fitted parameter.

performed by scanning the probe frequency for different delays.

The frequency of the saturating beam is fixed at 810 MHz (one Doppler width) from the center of the $^{22}$Ne line on the side opposite to the $^{20}$Ne line (the isotopic shift is 1652 MHz). Only $^{22}$Ne atoms can be directly pumped and the whole signal observed near the $^{20}$Ne central frequency is due to metastability-exchange collisions: $^{22}\mathrm{Ne}^* + {}^{20}\mathrm{Ne} \rightarrow {}^{22}\mathrm{Ne} + {}^{20}\mathrm{Ne}^*$. On the other hand the signal observed near the frequency of the saturation peak describes the direct collisions of $^{22}$Ne* with both isotopes and the exchange collisions with $^{22}$Ne. The latter contribution is small since we used a mixture with only 10% $^{22}$Ne.

Figure 2 shows the buildup of the saturated absorption collisional background as a function of the delay. It appears that the exchange signal is always very broad and exhibits a fast thermalization of velocities while the direct-collision signal is important mainly near the initial velocity. The curves shown in Fig. 2 suggest that the exchange kernel is wide and the direct kernel is narrow, but they cannot give their exact shape. Indeed, the relaxation rate of the saturated absorption peak after a short pulse[14] is 2 μs (at 20 mT). This means that the average time between two collisions strong enough to remove the atom out of the saturation peak is 2 μs; therefore, to observe the effect of one collision for each atom, it is necessary to record the saturation spectrum with a delay of the order of or less than 2 μs. This has been obtained by improving the signal-to-noise ratio: Figs. 3(a) and 3(b) show the background shapes observed for short delays (1.5 and 2 μs). These experimental curves directly represent the broad part of the kernel. There is a fair agreement with the theoretical shape. In addition, the existence of the narrow peak of the direct kernel has been demonstrated previously by the observation of the broadening of the saturation peak as a function of time.[7]

One major question, which will be discussed elsewhere, is the sensitivity of the kernel to the shape of the differential cross section. Preliminary calculations have shown that different test functions, for the differential cross section, produce very different kernels which would be in contradiction with the experiments.

In conclusion, we have achieved the complete connection from realistic potentials to the exchange and direct collision kernels, directly observed in our experiment. We have demonstrated the ability of our experimental method to provide the shape of the collision kernel and we plan to study other Ne*–noble-gas collision processes.

---

[1] V. A. Alekseev, T. L. Andreeva, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. 62, 614 (1972) [Sov. Phys. JETP 35, 325 (1972)].

[2] J. Ward, J. Cooper, and E. W. Smith, J. Quant. Spectrosc. Radiat. Transfer 14, 555 (1974).

[3] A. P. Kolchenko, S. G. Rautian, and A. M. Shalagin, unpublished.

[4] P. R. Berman, Adv. At. Mol. Phys. 13, 57 (1977), and and references therein.

[5] S. Avrillier, Ch. J. Brodé, J. Picart, and N. Tran Minh, in Proceedings of the Fifth Symposium on Spectral Line Shapes, Berlin, 1981 (to be published).

[6] J. Keilson and J. E. Störer, Q. Appl. Math. 10, 243 (1952). An example of interpretation with this kernel is given in C. Brechignac, R. Vetter, and P. R. Berman, J. Phys. (Paris), Lett. 39, L231 (1978).

[7] M. Gorlicki, A. Peuriot, and M. Dumont, J. Phys. (Paris), Lett. **41**, L275 (1980).

[8] P. R. Berman, T. W. Mossberg, and S. R. Hartmann, Phys. Rev. A **25**, 2550 (1982).

[9] J. S. Cohen and B. Schneider, J. Chem. Phys. **61**, 3230 (1974).

[10] I. Colomb de Daunant, G. Vassilev, G. Rahmat, and J. Baudon, J. Phys. B **13**, L711 (1980).

[11] W. Beyer, H. Haberland, and D. Hausamann, in Proceedings of the Eighth International Symposium on Molecular Beams, Cannes, 1981 (to be published), abstract p. 2-4.

[12] I. Colomb de Daunant, G. Vassilev, J. Baudon, and B. Stern, J. Phys. (Paris) **43**, 591 (1982).

[13] N. Courtier and M. Dumont, Rev. Phys. Appl. (Paris) **16**, 601 (1981)

[14] M. Dumont, M. Gorlicki, and F. Manzano, in Proceedings of the Second Conference on the Influence of Collisions on Spectral Line Shapes, Orléans, 1982 (to be published).

---

# Crossover Behavior of Transport Properties of Dilute Polymer Solutions

Y. Oono and M. Kohmoto

*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign,*
*Urbana, Illinois 61801*

(Received 10 September 1982)

The crossover behavior (temperature dependence) of universal ratios containing the intrinsic viscosity, the mean square radius of gyration, and the osmotic second virial coefficients is studied with use of the renormalization-group theory. The agreement with experimental results is satisfactory in some cases, but the wild scattering of existing experimental results calls for more accurate and systematic experiments.

PACS numbers: 36.20.Ey, 66.90.+r

Frictional properties of dilute polymer solutions, such as viscosity, sedimentation, and diffusion, are important in experimental characterizations of polymers.[1] The scaling theory initiated by de Gennes[2] has successfully given the asymptotic behavior of frictional properties[3] as well as static ones. However, the scaling theory[3] cannot give detailed information about the crossover behavior (e.g., the temperature dependence). It has been shown by Akcasu and Han,[4] Weill and des Cloizeaux,[5] and François, Schwartz, and Weill[6] with the aid of approximate theories that the dynamical properties converge very slowly to their asymptotic values. Therefore, the study of the crossover behavior is inevitable in understanding dilute polymer solutions. However, there have been no satisfactory theories to describe the Gaussian self-avoiding-chain crossover behavior. The extensively used (two-parameter theoretic) perturbative approach which is reviewed in Yamakawa's monograph[7] fails to explain the universal curves experimentally obtained, such as the plot of $A_2M/[\eta]$ vs $\alpha_S{}^2$ where $A_2$ is the osmotic second virial coefficient, $M$ the molecular weight, $[\eta]$ the intrinsic viscosity, and $\alpha_S{}^2 = \langle S^2\rangle/\langle S^2\rangle_{\text{theta}}$ with $\langle S^2\rangle$ being the mean square radius of gyration.

In a recent paper[8] we have calculated the asymptotic values of universal ratios containing frictional properties by using the conformation-space renormalization-group theory[9] with the $\epsilon$-expansion method, where $\epsilon = 4-d$, $d$ being the spatial dimensionality. Our estimates of asymptotic ratios are in reasonably good agreement with recent experimental results.

The purpose of this Letter is to present a renormalization-group–theoretical approach for the crossover behavior of the intrinsic viscosity. The $\epsilon$-expansion method is used to obtain systematic results, which are then compared with experimental data.

We calculate transport properties in the Kirkwood-Riseman scheme[10] *without preaveraging* the Oseen tensor. The transport coefficients are given by ensemble averages of quantities containing the force $\vec{F}(\tau)$ exerted by the solvent on the chain unit at the contour variable $\tau$. In the Kirkwood-Riseman scheme, $\vec{F}(\tau)$ obeys

$$\vec{F}(\tau) = \zeta_0\{\vec{u}(\tau) - \vec{v}[\vec{C}(\tau)]\} - \zeta_0\int_{|\tau-\tau'|>a} d\tau \int d\tau'\, \vec{T}(\tau,\tau')\vec{F}(\tau'), \qquad (1)$$

where $\zeta_0$ is the bare friction coefficient of the chain unit, $\vec{u}(\tau)$ is the velocity of the unit at $\tau$, $\vec{v}(\vec{r})$ is