accurate. This conclusion is only partially valid. First of all, over a wide range of velocities (v =1 to 5 a.u.) we find high degrees of relative s-p coherence $|\sigma_{sp}|/(\sigma_s\sigma_p)^{1/2}$ up to 0.98. Qualitatively, this agrees with experimental values $\lesssim 0.8$ of Ref. 6 in the case of beam-foil interaction. Similarly, the phase of σ_{sp} is confirmed by the phase of the difference beat signal. Because of the complicated dependence of the modulation depth of I^+ and the amplitude ratio $(I^+-I^-)/I^+$ on the relative cross sections σ_{pm}/σ_s, however, the fit in Fig. 1 does not allow a reliable estimate of these relative cross sections. For example, we have also found good fits to the data by inserting Shakeshaft's proton-hydrogen capture cross sections, determined within a seventy-coupled-states calculation,[7] but still using the OBK results for the degree and the phase of atomic coherence. Therefore, the agreement between experiment and theory should not be overestimated if one considers a relative cross sections in different substates. Further investigations concerning orientation and alignment[8] of the excited hydrogenic state after electron capture are in progress.

I wish to thank Professor Gabriel, Dr. Schröder, Dr. Kupfer, Professor Andrä, and A. Gaupp for many valuable suggestions and discussions. This work is supported by the Deutsche Forschungsgemeinschaft.

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Absorption Line-Narrowing Experiment between Atoms of Two Different Species

J. L. Picqué and R. Vetter
Laboratoire Aimé Cotton, Centre National de la Recherche Scientifique, 91405 Orsay, France
(Received 26 March 1979)

An experiment analogous to a three-level absorption line-narrowing experiment is performed between atoms of two different species (krypton and xenon) connected by a resonant excitation transfer. Results show that the hole burned in the velocity distribution of krypton atoms is transferred to xenon ones. This effect is interpreted by introducing a cross-collision kernel. Analysis of the experimental line shapes is consistent with a Gaussian shape of this kernel, whose width is found to be pressure independent.

Conventional absorption line-narrowing (ALN) experiments[1] involve a three-level system in atoms of a given species. A transition $a \leftrightarrow b$ is saturated by a first, intense laser beam, while the coupled transition $b \leftrightarrow c$ is probed by a second, weak laser beam [Fig. 1(a)]. The experiment which we describe in this paper is similar in principle to such an ALN experiment. However, it presents a fundamental difference: The saturated and probed transitions belong to atoms of *different species* (krypton and xenon, respectively). Here, the levels a of Kr and a' of Xe, connected by a resonant excitation transfer [Fig. 1(b)], play the role of the common level a of the usual three-level system. The remarkable feature that we have observed is that the *line-narrowing* effect remains. In other words, the hole burned in the longitudinal velocity distribution of the level a of Kr atoms gives rise through the excitation-exchange process to a hole in the level a' of Xe atoms. It is to be noted that the radiation fields cannot induce coherence between the levels b and c' of the pseudo three-level system of Fig. 1(b). This results in a simpler theoretical expression of the signal than in the case of the true three-level system of Fig. 1(a).

Our experiment can also be compared to a two-level saturated absorption experiment in the presence of foreign perturber atoms. In such an experiment, the same "active" atoms experience both the saturating and the probe fields. In a recent work of this type,[2] the modification of the

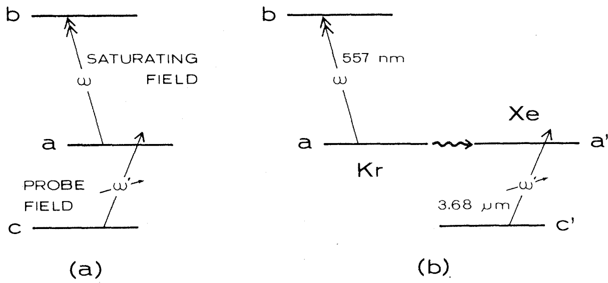

FIG. 1. Diagrams of relevant level: (a) in a conventional three-level ALN experiment, (b) in the present experiment involving atoms of two different species connected by a resonant excitation transfer.

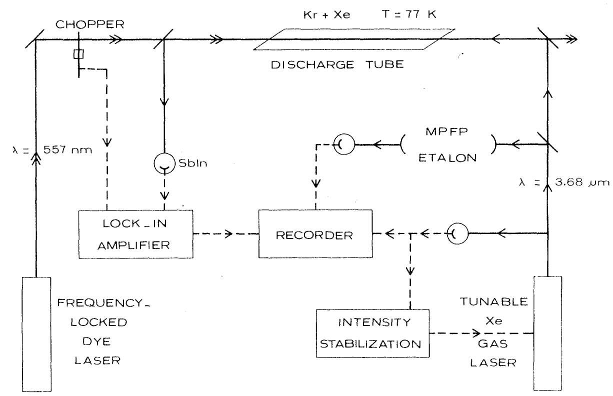

FIG. 2. Simplified scheme of the experimental setup. The auxiliary saturated-absorption arrangement used for locking the dye-laser frequency is not shown. MPFP denotes multipath Fabry-Perot etalon.

nonequilibrium narrow velocity distribution of the active atoms through a succession of elastic collisions with perturber atoms having the thermal equilibrium velocity distribution was investigated. The results were interpreted with the aid of a collision kernel connecting the velocities of the active atom before and after the collision. In the present experiment, however, the saturating field and the probe field act on different atoms. We look at the shape of the velocity distribution induced in "energy-acceptor" atoms (Xe) in thermal equilibrium through transfer collisions with "energy-donor" atoms (Kr metastables) having a narrow nonequilibrium velocity distribution. To explain our results, we have introduced a *cross-collision kernel* involving the two atomic species. While in the above-cited saturated-absorption experiment the active atom underwent a large and undetermined number of elastic collisions, we observe here the effect of a *single* excitation-transfer collision. This allows a further simplification of the interpretation of the experiment.

The relevant energy levels in our experiment have the cascade configuration shown in Fig. 1(b). The saturated transition $a \leftrightarrow b$ connects the metastable level $4p^5 5s[\frac{3}{2}]_2$, highly populated in a discharge, to the upper level $4p^5 5p'[\frac{1}{2}]_1$ of ^{86}Kr. The probe transition $a' \leftrightarrow c'$ couples the resonant level $5p^5 5d[\frac{1}{2}]_1$ to the lower excited level $5p^5 6p[\frac{1}{2}]_1$ of ^{136}Xe. Because the energy difference between the facing levels a and a' (15 cm^{-1}) is much less than the thermal energy $k_B T$ (55 cm^{-1} at $T = 77$ K), we are allowed to regard the excitation transfer as resonant.[3] Another advantage of the system (related to this quasiresonant character) is the large transfer cross section,[4] which yields a good signal-to-noise ratio in the experiment. Thanks to the technique of modulation described below, the only Xe atoms which contribute to the signal are those resulting from transfer collisions with the velocity-selected metastable Kr atoms.

The experimental arrangement is shown in Fig. 2. The ^{136}Xe and ^{86}Kr atoms are held in a discharge tube cooled at liquid-nitrogen temperature. The saturating beam is provided by a cw single-mode dye laser, locked to a fixed frequency near the Kr line $a \leftrightarrow b$ at $\lambda = 557$ nm. It is intensity modulated with a mechanical chopper. A counter-propagating probe beam[5] is provided by a cw single-mode Xe gas laser oscillating on the infrared line $a' \leftrightarrow c'$ at $\lambda = 3.68$ μm, finely tunable across its gain curve. The modulated part of the probe absorption signal is detected with a lock-in amplifier, whose dc output is recorded as the Xe laser frequency is swept.

A typical recording of the probe profile, performed at a low Kr partial pressure and with the saturating laser at exact resonance, is shown in Fig. 3. The 34-MHz width [full width at half maximum (FWHM)] of this profile is significantly smaller than the 50-MHz width of the Voigt profile which would be observed if the "transferred" population of the level a' of Xe were thermalized. In fact, the observed width falls approximately halfway between this linear-absorption width and the width $\Gamma_{a'c'} + (k'/k)\Gamma_{ab} \simeq 14$ MHz expected for a true three-level system[1] ($\Gamma_{a'c'}$ and Γ_{ab} are the homogeneous widths of the probe and saturated transitions, respectively, k' and k are their wave numbers).

For the theoretical interpretation of the experiment, we have found it convenient to define a cross-collision kernel $W(V_z \rightarrow v_z')$, which repre-

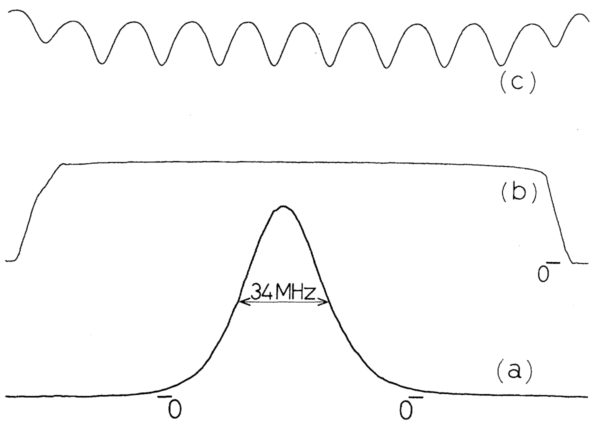

FIG. 3. Trace (a), typical recording of the probe signal (saturator detuning, $\Delta = 0$; temperature, 77 K; Kr pressure, 17 mTorr; trace (b), output level of the frequency scanning Xe laser; trace (c), MPFP reference fringes (here inverted), separated by 20.85 MHz.

sents the probability density per unit time for a donor of longitudinal velocity V_z to give rise through an excitation-exchange collision to an acceptor of longitudinal velocity v_z'. In the usual semiclassical density-matrix formalism, the equations of motion of the two-atom system can then be written as for two independent atoms, respectively, interacting with a quasiresonant radiation. Because of the low partial pressure of Xe used throughout our experiments, we can reasonably assume that the transfer does not modify the population ρ_{aa} of the Kr metastable level a. Thus the only addition to the case of two independent atoms is the following population term in the equation which governs the time evolution of the population $\rho_{a'a'}$ of the Xe level a':

$$[d\rho_{a'a'}(v_z';t)/dt]_{\text{tr}} = \Gamma \int W(V_z \to v_z')\rho_{aa}(V_z,t)\,dV_z \quad (1)$$

(Γ is the total rate of excitation-exchange collisions). The steady-state solution of the complete set of equations, in the linear approximation for the weak probe field, yields the following shape of the signal:

$$S_\Delta(\Delta') \propto \int dv_z' \frac{1}{(\Delta' + k'v_z')^2 + \frac{1}{4}\Gamma_{a'c'}^2} \times \int dV_z W(V_z \to v_z') \frac{\exp-(V_z^2/U^2)}{(\Delta - kV_z)^2 + \frac{1}{4}\Gamma_{ab}^2}. \quad (2)$$

Here $\Delta' = \omega' - \omega_{a'c'}$ and $\Delta = \omega - \omega_{ab}$ are the detunings of the probe and saturating fields, respectively, and U is the most probable velocity of the donors' thermal distribution. Expression (2) includes the special case of the true three-level system in a single atom (with population effects only) for $W(V_z \to v_z') = \delta(v_z' - V_z)$, and that of the thermalized transferred population for $W(V_z \to v_z') \propto \exp[-(v_z'^2/u^2)]$ (u is the most probable velocity of the acceptors' thermal distribution).

Very few data can be found in the literature concerning velocity changes occurring in resonant excitation transfers, especially for a non-Maxwellian initial velocity distribution. Let us consider the simple model of hard-sphere collisions between atoms constrained to move in one dimension. From the conservation of momentum and energy in the collision, we obtain, as a function of its initial velocity v, the final velocity v' of an acceptor (mass m) colliding with a donor (mass M) with initial velocity V:

$$v' = [(m - M)/(m + M)]v + [2M/(m + M)]V. \quad (3)$$

For a Maxwellian distribution, $f(v) \propto \exp[-(v^2/u^2)]$, of the acceptor velocities, the cross kernel is readily derived:

$$W(V \to v') = \int dv f(v) \delta\left(v - \frac{m+M}{m-M}\left[v' - \frac{2M}{m+M}V\right]\right) = (\pi^{1/2}\delta u)^{-1} \exp\{-[(v' - \beta V)^2/(\delta u)^2]\}, \quad (4)$$

with $\delta u = u(m - M)/(m + M)$ and $\beta = 2M/(m + M)$, i.e., $\delta u \simeq \frac{1}{4}u$ and $\beta \simeq \frac{3}{4}$ for Xe acceptors and Kr donors. In their kinetic aspect, the conservation laws applying to the collision process are the same for resonant excitation-exchange collisions as for elastic ones. By performing numerical calculations on hard-sphere elastic collisions, Borenstein and Lamb have shown how one-dimensional Gaussian kernels, describing velocity changes internal to a given atom, can be extrapolated to three-dimensional ones.[6] For the cross kernel considered here, such a generalization is expected to increase δu and decrease β.

From such physical arguments and from systematic analysis of the experimental line shapes under various conditions, we have been led to choose a phenomenological cross kernel in the simple form

$$W(V_z \to v_z') = (\pi^{1/2}\delta u)^{-1} \times \exp\{-[(v_z' - \beta V_z)^2/(\delta u)^2]\}. \quad (5)$$

One can verify easily that

$$\langle v_z'\rangle = \int W(V_z \to v_z')\, v_z'\, dv_z' = \beta V_z\,, \tag{6a}$$

$$\langle (v_z' - \langle v_z'\rangle)^2\rangle = \tfrac{1}{2}(\delta u)^2. \tag{6b}$$

Therefore, βV_z and δu represent the mean and the dispersion, respectively, of the velocity distribution of the acceptors having collided with a donor with initial velocity V_z. The case of the true three-level system appears as equivalent to the limit of complete transfer of the donors' velocities ($\delta u = 0$, $\beta = 1$) and the case of the thermalized transferred population as equivalent to the limit of unchanged velocities ($\delta u = u$, $\beta = 0$).

For the purpose of evaluating δu, we have first recorded a series of probe profiles with the saturating laser at exact resonance ($\Delta = 0$), for various Kr partial pressures in the range 0–200 mTorr and with a fixed Xe pressure (3 mTorr, determined by the bath temperature). The widths of these profiles are plotted in Fig. 4 [curve *a*]. We have determined independently the homogeneous widths $\Gamma_{a'c'}$ and Γ_{ab}, by means of auxilliary experiments performed under the conditions of the main experiment, in the same discharge tube: $\Gamma_{a'c'}$ was measured by linear absorption[7] (with the dye laser turned off) and Γ_{ab} by saturated absorption[8] (with the Xe laser turned off and a counterpropagating beam provided by the dye laser). These measurements indicate that $\Gamma_{a'c'}$ varies linearly [curve *b*] with the Kr pressure

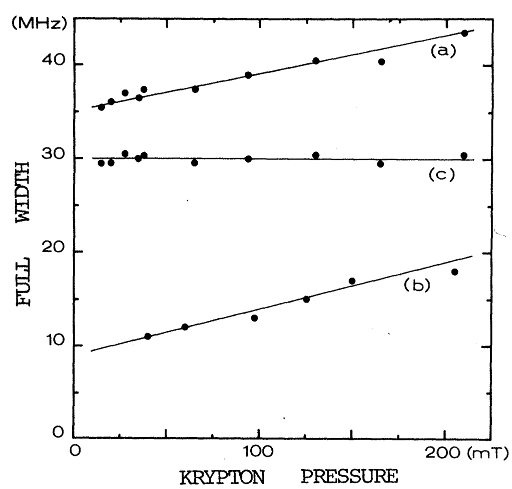

FIG. 4. Plot of full widths at half maximum (*n* with an unceraintiy of 1 MHz) as a function of the Kr pressure: curve (a), experimental width of the probe signal; curve (b), experimental homogeneous width $\Gamma_{a'c'}$ of the probe transition; curve (c), deduced width of the cross collision kernel.

(because of phase-interrupting Xe-Kr collisions), whereas Γ_{ab} is practically constant around 25 MHz (including power broadening). The experimental probe profiles are found to be consistent with the theoretical line shapes obtained by inserting the Gaussian kernel (5) into expression (2) and accounting for the experimental values of $\Gamma_{a'c'}$ and Γ_{ab}. The width of the kernel, as deduced from this profile analysis, is plotted in Fig. 4 [curve *c*]. It appears to have a *constant value* of 30 ∓ 1 MHz, whereas the Doppler width is 45 MHz.[9] Thus, $\delta u = \frac{2}{3}u$, i.e., the collision-induced velocity dispersion is *two-thirds* of that corresponding to the thermal distribution of Xe at 77 K.

Recordings have also been performed with the saturating laser tuned off resonance ($\Delta \neq 0$). We have observed in this case a slight shift of the probe signal. Typically, when detuning the dye laser by $\Delta = 200$ MHz (about half the Doppler width of the Kr line), we observed a shift $\delta \simeq 4$ MHz. Through the relation $\delta = \beta(k'/k)\Delta$, this corresponds to $\beta \simeq 0.1$. Although the effect is rather small, it shows that transfer collisions do not completely destroy the memory of donors' velocities. Therefore, for both β and δu, the behavior of transfer collisions is found to be intermediate between the two extreme cases of hard-sphere collisions and velocity-unchanging collisions.

In conclusion, the ALN-type experiment described in this paper has revealed the importance of velocity effects in excitation-exchange phenomena. Our approach utilizing a simple cross-collision kernel[10] should prove fruitful in the understanding of more conventional resonant or nonresonant transfer experiments.[11] The fact that the width of the kernel has been found to be pressure independent constitutes a good check of the validity of this model. Finally, our work suggests the possibility, for well-suited species, to create large population inversions in narrow frequency bands via excitation-exchange processes.

[1]Concerning three-level experiments and related theory, see, e.g., I. M. Beterov and V. P. Chebotaev, in *Progress in Quantum Electronics*, edited by J. H. Sanders and S. Stenholm (Pergamon, Oxford, 1974), Vol. 3, Pt. 1, and references therein.

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[3]In fact, since the transfer is slightly endothermic ($\Delta E = -15$ cm^{-1}), it could lead by itself to an acceptor velocity distribution narrower than the thermal one. In a complementary linear absorption experiment (without saturating beam) performed on Xe atoms in the presence of Kr metastables, we indeed observed a slightly reduced width. However, in the nonlinear absorption experiment, this pure kinematic cooling effect can be neglected compared to the laser-induced narrowing effect.

[4]From the data of J. E. Velazco, J. H. Kolts, and D. W. Setser [J. Chem. Phys. 69, 4357 (1978)], this cross section can be estimated to be from 30 to 40 Å^2.

[5]We have also performed experiments with copropagating light beams. The two geometries yield the same line shapes, thus confirming the absence of the anisotropic coherence term in the expression of the signal.

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[9]Of course, these two widths depend on the temperature. We have made most observations at 77 K for reasons of experimental convenience.

[10]A usual kernel of the type $W(v_z \to v_z')$, connecting the initial and final velocities of the acceptors (Refs. 2 and 6), could also have been used. However, such a kernel seems less adapted to the present problem since its shape would depend on the donors' velocity distribution, and hence of the conditions specific to each experiment.

[11]See, e.g., J. Brochard and R. Vetter, J. Phys. (Paris) 38, 121 (1977).

Numerical Solution of the Time-Dependent Schrödinger Equation and Application to H^+-H

Vida Maruhn-Rezwani, Norbert Grün, and Werner Scheid
Institut für Theoretische Physik der Justus-Liebig-Universität Giessen, Giessen, West Germany
(Received 23 May 1979)

The time-dependent Schrödinger equation for the motion of the electron in a H^+-H collision is solved numerically with a finite-difference method on an axially symmetric spatial mesh. Sample density distributions for $E_{\rm lab} = 20$ keV are shown. The calculated charge-transfer probabilities at $E_{\rm lab} = 3.92$, 7.69, and 20.1 keV are in good agreement with experiment.

The usual procedure in atomic collision problems is to expand the wave function in a basis set.[1] Even for velocities which allow a classical treatment of the nuclear motion,[2] the success of a calculation depends on the selection of a necessarily finite expansion basis. In principle one should be able to describe different effects like excitation, charge transfer, and ionization with the same basis set. Particularly, charge transfer involves a correct inclusion of the electron translational effects,[3] and ionization the knowledge of continuum functions for the two-center Coulomb problem.[4] Furthermore, the choice of a suitable basis set for the intermediate-velocity region, where neither an atomic expansion nor a molecular one is adequate, seems to be difficult.

For nulcear collision problems the numerical integration of the time-dependent Hartree-Fock equations was recently carried out and applied to heavy-ion scattering.[5-8] It seems worthwhile to try a similar method also in atomic physics in order to circumvent the difficulties sketched above. However, from the very beginning one should be aware of the different nature of the nuclear and atomic problem. All potentials in atomic physics are known to be of Coulombic type. Unlike the nuclear potentials, they have singularities at the positions of the charges and, further, have an infinite range which requires special numerical care. In the case of atomic collisions the difficulties in the calculation of the cross sections would be less stringent than in nuclear physics since the final states are more easily definable. Both theoretical fields have not yet fully answered the question to what extent a time-dependent Hartree-Fock theory gives the correct description of the collision process.

In order to gain experience in handling the atomic problem we start with the time-dependent one-electron problem and solve the Schrödinger equation of an electron in the Coulomb field generated by two moving nuclei. In the following we consider the H^+-H scattering. Then the Schrödinger equation is given by

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r},t) - \left(\frac{e^2}{|\vec{r}-\vec{r}_1(t)|} + \frac{e^2}{|\vec{r}-\vec{r}_2(t)|}\right)\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t). \qquad (1)$$

