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Binary formation of NaNe quasibound molecules observed in spin relaxation of Na

F. A. Franz and A. Sieradzan*
Department of Physics, Indiana University, Bloomington, Indiana 47405

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Quasibound NaNe molecules are shown to contribute strongly to the spin relaxation of Na optically pumped in the presence of Ne. Molecules formed in two-body (tunneling) collisions are distinguished from those formed in three-body collisions. The cross section for the collisional breakup of the quasibound complexes has been measured to be 3×10^{-13} cm^2.

The application of laser optical pumping of Na to the generation of polarized nuclear targets and ion sources,[1,2] the observation that nuclear-fusion reaction rates can be altered through the use of spin-polarized nuclei,[3] and the realization that polarization of heavy noble-gas nuclei through spin exchange with polarized alkali-metal atoms occurs mainly through intermediate formation of van der Waals molecules[4-7] have renewed interest in understanding the processes which affect the degrees of spin polarization attainable in optically pumped vapors. We report evidence from a laser optical-pumping experiment which shows that the electronic spin relaxation of Na in the presence of Ne at low pressure is dominated not by sudden binary collisions as has long been assumed, but rather by the formation of NaNe van der Waals molecules. Effects of quasibound molecules formed in two-body tunneling collisions are differentiated from those of molecules formed in three-body collisions; quasibound molecules turn out to play a particularly important role in the relaxation process, providing unique insights into the dynamics of van der Waals molecular formation.

The probability that an alkali-metal atom will suffer electronic spin relaxation in a sudden binary collision with a noble-gas atom is remarkably small; cross sections for this process in the $^2S_{1/2}$ ground state of Na range from 10^{-20} to 10^{-25} cm^2.[8,9] As a result, far rarer and more infrequent collisional interactions can make significant contributions to relaxation if these interactions last for a particularly long time, or if they are particularly strong. The influence of van der Waals molecular formation upon Rb spin relaxation in the noble gases is an example; relatively long-lived molecular states dominate relaxation despite the fact the rates of molecular formation are orders of magnitude smaller than the rates of ordinary binary collisions.[10]

van der Waals molecular formation might be expected to have negligible influence on the spin relaxation of Na in Ne, however. Molecular formation rates for Na atoms in He or Ne should be far smaller than those for Rb in Kr or Xe, due to the substantially smaller depth of the van der Waals potential minimum for alkali-metal atoms in the light noble gases.[11] The strengths of the interaction responsible for relaxation in the molecular state (an induced spin-orbit interaction, $\gamma(\vec{S}\cdot\vec{N})$, the same interaction responsible for relaxation in sudden binary collisions) are orders of magnitude smaller for Na in He or Ne than for Rb in Kr or Xe.[12] Nevertheless, the formation of NaNe van der Waals molecules yields macroscopic spin-relaxation rates of Na which are as much as a hundred times greater than the relaxation rates arising from sudden Na-Ne collisions.

We have performed two experiments in which molecular contributions to electronic spin relaxation of Na in Ne have been isolated. Both experiments involve the generation of electronic ($\langle S_z \rangle$) and nuclear ($\langle I_z \rangle$) spin polarizations of $3^2S_{1/2}$ Na atoms through the absorption of circularly polarized $3^2S_{1/2} \rightarrow 3^2P_{1/2}$ light (optical pumping).[12] The experimental observables are the pumping and relaxation transients, both of which monitor $\langle S_z(t) \rangle$. The transients are affected by rates of spin relaxation arising from collisions of Na atoms with the walls of the experimental cell, sudden binary collisions of Na with Ne, electronic spin-exchange collisions of Na with Na, and collisions resulting in the formation of NaNe molecules. Most collisional interactions act directly upon the electronic spins of Na atoms, with subsequent nuclear (and electronic) spin reorientation occurring through the hyperfine interaction in the time between collisions. This decoupling-recoupling interaction gives rise to an $\langle S_z(t) \rangle$ transient in low magnetic field which is the sum of two exponential terms with rate constants Z_2 and Z_1, respresenting, approximately, the relaxation rates for $\langle S_z \rangle$ and $\langle I_z \rangle$. The ways that various relaxation mechanisms contribute to Z_2 and Z_1 are well established, allowing the determination of individual relaxation rates through measurement of the dependence of Z_2 and Z_1 upon alkali-metal density, noble-gas pressure, magnetic field, etc.[13]

We were searching for an anomalous mode of relaxation (R^*) discovered earlier for Rb in He which has been attributed to the modification of the Rb hyperfine interaction, $\delta a(\vec{S}\cdot\vec{I})$, in Rb-He van der Waals molecules. A unique signature of $\delta a(\vec{S}\cdot\vec{I})$ relaxation is that, no matter how strong a contribution it makes to Z_2, a *zero* contribution is made to Z_1. Discovery of R^* led to the resolution of numerous ambiguities and disagreements in earlier determinations of Rb relaxation cross sections, but its attribution to molecular effects was not definitely established.[13,14]

Our first experiment was performed at low magnetic field in a conventional optical pumping rig. Weak circularly polarized D_1 (5896 Å) light impinged on an experimental cell (6.10-cm length, 3.45-cm radius) containing Na and Ne at 115 °C; pumping transients were monitored and averaged by measuring the response of the transmitted light intensity to the gating of rf power which saturated the ground-state Zeeman resonance. In Fig. 1 we display measurements of Z_1 and Z_2, for Na as a function of pressure of Ne. The fit of a theoretical expression for Z_1 (Ref. 13) to the data yields 0.49 cm^2/sec for the diffusion coefficient of Na in Ne (0.28 cm^2/sec extrapolated to 273 K), and 1.4×10^{-23} cm^2 for the nuclear-spin-independent cross section for $\gamma(\vec{S}\cdot\vec{N})$ relaxation in sudden binary collisions of Na and Ne. Both values

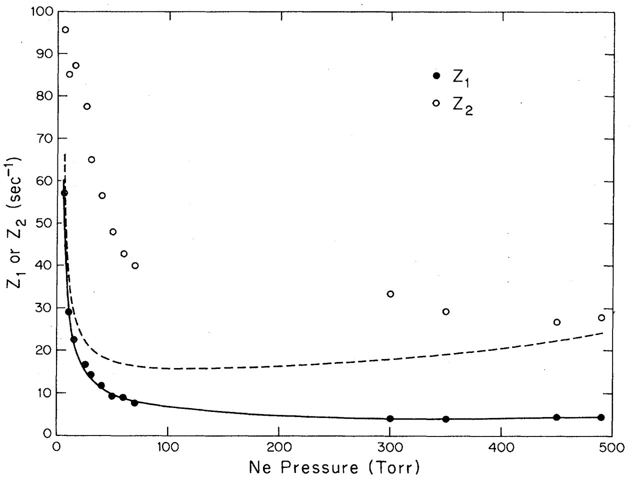

FIG. 1. Measured pumping-relaxation rates Z_1 and Z_2 for Na in Ne. The solid line is a fit to the Z_1 data determining the diffusion coefficient of Na in Ne and the cross section for $\gamma(\vec{S}\cdot\vec{N})$ relaxation in sudden binary collisions of Na with Ne. The dashed line is a projection of Z_2 values based on these parameters. The actual measurements of Z_2 are higher than the projection because of the presence of NaNe molecular relaxation.

are in good agreement with previous measurements.[15-17] The dashed line represents the projection of Z_2 values based upon these parameters. The extraordinary disagreement of the projection with the measured values of Z_2 is due to the presence of R^* contributions to Z_2 which have not yet been included. Calculations of the amounts of R^* required to bring calculations of Z_2 into agreement with the measured values yield the data in Fig. 2. In the region below 15 Torr these contributions of R^* are more than 100 times greater than the relaxation rate from ordinary binary collisions.

If the attribution of R^* to $\delta a(\vec{S}\cdot\vec{I})$ relaxation in NaNe van der Waals molecules is correct, the following theoretical description should apply:[14,18]

$$R^* = \frac{8\pi^2}{3}\frac{\langle\delta a\rangle^2\tau_{e1}\tau_{e2}I(I+1)T_f^{-1}}{1+\tau_{e2}^2\Delta W^2} \ , \qquad (1)$$

where τ_{e2} is the correlation time for the perturbation, τ_{e1} is the duration of the perturbation, $\langle\delta a\rangle$ is the average shift in the Na hyperfine constant a per perturbation, I is the nuclear spin, ΔW is 2π times the separation between hyperfine states, and T_f^{-1} is the formation rate of complexes.

The manner in which NaNe molecules are formed is reflected in the pressure dependence of T_f^{-1}. Three-body Na-Ne-Ne collisions can result in a NaNe bound state (or quasibound state); T_f^{-1} is proportional to p^2. Two-body collisions of Na with Ne of the appropriate energy and angular momentum can result in tunneling through the centrifugal barrier to a quasibound NaNe state; in this case T_f^{-1} is proportional to p.[11] Equation (1) indicates that at high pressures p^2 dependence of the three-body formation rate is canceled by the p^{-2} dependence of $\tau_{e1}\tau_{e2}$; R^* in such a case should approach a constant value. The linear pressure dependence of the two-body formation rate, however, leads to a maximum in R^*, with R^* falling to zero at high p. Inspection of the data in Fig. 2 suggests that R^* effects in NaNe are almost entirely due to two-body formation of complexes, that is, to formation of quasibound molecular states through tunneling. We know of no other experiment which distinguishes so clearly between two- and three-body van der Waals molecular formation.

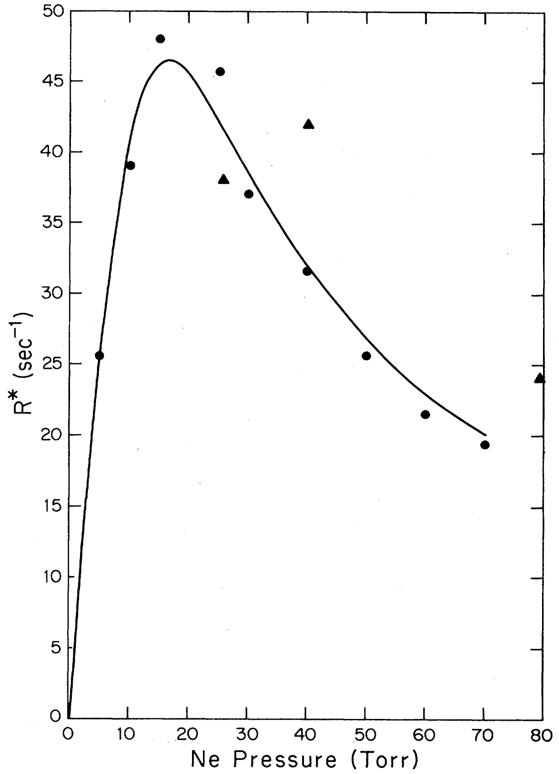

FIG. 2. NaNe molecular relaxation rate vs Ne pressure at low magnetic field, as determined from measurements of Z_2. ●'s are weak pumping measurements; ▲'s are laser pumping measurements.

In fitting Eq. (1) to the R^* data we found no significant distinction between τ_{e1} and τ_{e2}; we take

$$\tau_{e1}^{-1} = \tau_{e2}^{-1} = \tau_0^{-1} + n_0\sigma_B v_{\mathrm{rel}}\,p/p_0 \ , \qquad (2)$$

where n_0 is Loschmidt's number, σ_B is the breakup cross section for the quasibound complexes, v_{rel} is the mean relative velocity of Na atoms and Ne atoms, p is the Ne pressure, and p_0 is atmospheric pressure. Fits also indicate that the average natural lifetime τ_0 of the quasibound complex is sufficiently long that both τ_{e1}^{-1} and τ_{e2}^{-1} are determined solely by the collisional breakup rate. The best fit to the data, indicated by the solid line in Fig. 2, yields

$$\sigma_B = 3.2\times10^{-13}\ \mathrm{cm}^2, \quad \langle\delta a^2\rangle T_f^{-1} = 7.2\times10^{18}\ \mathrm{psec}^{-3} \ .$$

This cross section is about an order of magnitude larger than the cross section for the breakup of truly bound van der Waals molecules. If we assume that the shift in "a" in a quasibound state can be as much as 10% of a, that implies a formation rate of 900 psec^{-1}, not an unreasonable number based on the known NaNe potentials.[19,20]

It may seem surprising that an effect as large as that displayed in Figs. 1 and 2 was not observed in earlier experiments. The reasons are simple; measurements either were made under conditions where only Z_1 was monitored,[9] to which R^* makes no contribution at all, or at He or Ne pressures significantly beyond the region of present interest[15, 17] where the p^{-2} dependence of the square of the correlation time overwhelms the p dependence of the formation rate, forcing R^* to fall to zero.

A conclusive test of the molecular origin of R^* is the measurement of the dependence of the strength of R^* upon magnetic field. Equation (1) predicts that as ΔW increases, R^* should diminish. Molecular correlation times should be orders of magnitude longer than correlation times for sudden binary collisions; based on the breakup rate above, a significant decrease in R^* should occur at about 1 kG for Na in 40 Torr of Ne, if R^*, in fact, is molecular in origin. In our second experiment we used laser optical pumping and detection to measure Na relaxation as a function of magnetic field up to 20 kG. The output from an argon-ion laser drove two dye lasers, one tuned to ~ 5896 Å (the D_1 pumping beam), and the other to ~ 5890 Å (the D_2 detection beam) at each value of the magnetic field. The chopped pumping beam passed into a small sealed cell (2.50-cm length, 1.05-cm radius) containing Na in 40 Torr of Ne maintained at 115 °C in the room-temperature access bore of a superconducting solenoid. The detection beam passed in the opposite direction through the cell onto the slit of a monochromator. Signal-averaging techniques were employed. Laser measurements at low magnetic field yielded results consistent with the weak pumping results already discussed, as we indicate by solid triangles in Fig. 2.

Measurements of R^* as a function of magnetic field are shown in Fig. 3; molecular relaxation is the only interaction present in this experiment that is expected to have this sort of dependence on magnetic field. In order to fit Eq. (1) to the data, we have approximated ΔW as 2π times the separation between the (2,0) and (1,0) states. [While at low magnetic fields ΔW is approximately the same for all states coupled by the $\delta a(\vec{S}\cdot\vec{I})$ interaction, in intermediate fields it depends upon the m values of those states.] The fit in Fig. 3 yields $\sigma_B = 1.9\times10^{-13}\ \mathrm{cm}^2$ and $\langle\delta a\rangle^2 T_f^{-1} = 5.1\times10^{18}$ psec^{-3}, both values in reasonable agreement with the previous results, offering conclusive proof of the molecular nature of anomalous relaxation.

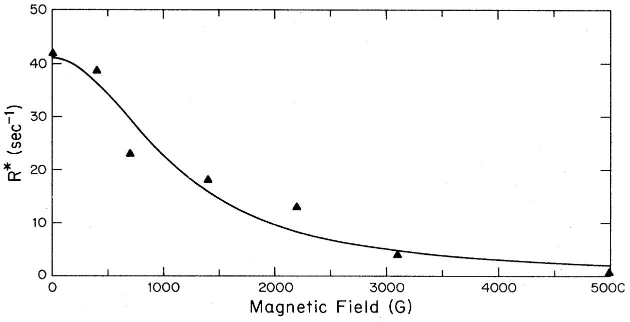

FIG. 3. NaNe molecular relaxation rate vs magnetic field.

Of several questions which remain, one is why R^* is not affected by a scale factor dependent upon magnetic field. It is this factor which allows the $\delta a(\vec{S}\cdot\vec{I})$ interaction in sudden binary collisions (the origin of the well-known pressure shift of the hyperfine interaction) to yield negligible relaxation in low H_0 but substantial relaxation at high H_0.[18] Our data and analyses suggest that R^* behaves as if a strong effective local magnetic field is present in the molecular state. For present purposes we have taken the scale factor to be 1, but more substantial consideration of this assumption clearly is warranted.

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[*] Present address: Department of Physics, Central Michigan University, Mt. Pleasant, MI 48859.

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