berg, and K. H. Speidel, Phys. Lett. 55B, 56 (1975).
[4]M. B. Goldberg, G. J. Kumbartzki, K.-H. Speidel, M. Forterre, and J. Gerber, to be published.
[5]F. Bosch and O. Klepper, Z. Phys. 240, 153 (1970).
[6]O. Klepper and W. Salm, to be published.
[7]O. Klepper, H. Spehl, and N. Wertz, Z. Phys. 217, 425 (1968); H. Spehl and N. Wertz, Z. Phys. 243, 431 (1971).
[8]H. Kopfermann, *Nuclear Moments* (Academic, New York, 1958).
[9]E. J. McGuire, Phys. Rev. 185, 1 (1969).
[10]J. D. Garcia, R. J. Fortner, and T. M. Kavanagh, Rev. Mod. Phys. 45, 111 (1973).
[11]M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972).

Velocity Dependence of Na-Ar and Na-Xe Fine-Structure-Changing Collisions*

Jerome Apt and David E. Pritchard
Research Laboratory of Electronics and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 2 February 1976)

The velocity dependence of the total fine-structure-changing cross section has been measured for collisions of Na($3p$) with Ar and Xe using a new velocity-selection technique based on the Doppler shift. The velocity dependence agrees with recent theoretical predictions of Pascale and Olson, but the magnitudes of the cross sections do not.

We report measurements of the velocity dependence of the fine-structure-changing cross section in collisions of excited sodium with the ground-state rare gases Ar and Xe, e.g.,

$$\mathrm{Na}^*(3p_{3/2})+\mathrm{Ar}\rightleftharpoons\mathrm{Na}^*(3p_{1/2})+\mathrm{Ar}+\Delta E\,,$$

where $\Delta E = 17\ \mathrm{cm}^{-1}$. These measurements are the first systematic study of the velocity dependence of this simple inelastic collision process in an alkali–rare-gas system (except for the elegant temperature-dependent measurements of Gallagher on Rb and Cs collisions[1]) and they are sufficiently accurate to discriminate among recent theoretical calculations of the Na–rare-gas cross sections.[2-4] The measurements are the first to apply our recently proposed technique of velocity selection using the Doppler shift (VSDS)[5] which uses one interaction of the laser field with the system under study to provide velocity-selective excitation; previous VSDS techniques have used two laser-system interactions to select and monitor the initial velocity[6] or the momentum transfer.[7,8]

In the VSDS technique monochromatic laser light is used to excite selectively atoms with a definite component of velocity, v_z, along the laser beam:

$$v_z = c(\Delta\nu/\nu_0) = \lambda_0\Delta\nu\,, \qquad (1)$$

where $\Delta\nu$ is the detuning of the laser frequency from the natural frequency of the atomic resonance, ν_0. The number of excited-state atoms is determined from the total fluorescence, $F_b(\Delta\nu)$, and the number of atoms transferred to the unexcited fine-structure level is determined from the fluorescence of that level, $F_t(\Delta\nu)$. In our experiment $F_t \ll F_b$ so that the average transfer coefficient at fixed v_z could be found from

$$\langle v_{\mathrm{rel}}Q(v_{\mathrm{rel}})\rangle_{v_z} = F_t(\Delta\nu)/F_b(\Delta\nu)\tau_{\mathrm{Na}}n_x\,, \qquad (2)$$

where τ_{Na} is the excited-state lifetime of the laser-excited state and n_x is the density of the rare-gas target. The notation $\langle v_{\mathrm{rel}}Q(v_{\mathrm{rel}})\rangle_{v_z}$ emphasizes that the relative velocity is affected by the unselected components of velocity of the primary and target atoms even though v_z is accurately known [from Eq. (1)].

The experiment was conducted in a heated aluminosilicate glass tube 8 mm i.d., which was suspended in a vacuum vessel (see Fig. 1). The

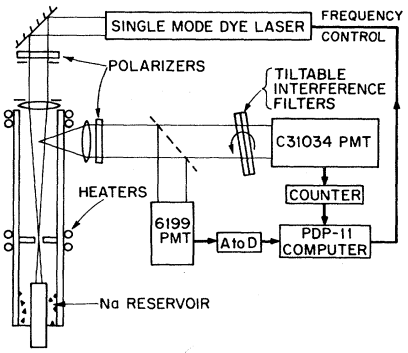

FIG. 1. Schematic view of apparatus. The C31034 (6199) photomultiplier detects the transfer (total) fluorescence.

rare-gas pressure was measured by both a thermocouple gauge and a trapped McLeod manometer. Laser light entered through a sapphire window at one end and excited through a hole in a stainless steel plug at the other end. This hole led to a separately heated sodium reservoir which was sealed off during the experiment allowing us to achieve a high temperature without paying the price of radiation trapping.

The light source was a Spectra Physics 580 single-mode dye laser, operated with rhodamine 6G; additional electronics stabilized the laser power and frequency. The laser output was attenuated (typically to $\lesssim 1$ mW) in order to eliminate both velocity-selective[9] and bulk[10] optical pumping.

Fluorescence from the center of the tube was collected at 90° to the laser beam with $f/1$ optics mounted in the pressure vessel and expanded to a 2-in.-diam beam with divergence of less than 20 mrad. A linear polarizer was oriented at 35° to the laser beam to eliminate the effect of any velocity-dependent alignment produced in the collisions.[9] A tilted glass reflected ~10% of the light into the total fluorescence detector, an RCA 6199 photomultiplier. Two three-cavity interference filters provided 1000:1 selection of the transfer fluorescence which was subsequently detected by a cooled RCA C31034 photomultiplier. (The filters could be tilt tuned to either line.)

The total and transfer fluorescence signals were recorded by a PDP-11/20 computer interfaced to the experiment. The computer also stepped the laser's frequency repeatedly across the Doppler profile in 0.5-GHz steps (the cavity mode spacing) at a rate of 1.5 sec per step. After each sweep over the line, the cavity length was changed slightly to shift the comb of cavity mode frequencies, and thereby access slightly different frequencies on subsequent sweeps across the Doppler profile. The line was swept roughly 15 times in the course of a 10-min run at one pressure and filter/laser line setting. Typical results for the total fluorescence are shown in Fig. 2.

Our overall procedure for measuring the velocity dependence of the rate coefficient $\langle v\, Q(v)\rangle_{v_z}$ was to make a run on both the $p_{3/2} \rightarrow p_{1/2}$ and $p_{1/2} \rightarrow p_{3/2}$ processes at a series of fixed pressures. The rare-gas pressure was varied in increments of roughly 50 mTorr from less than 0.1 up to 500 mTorr, and $\langle v\, Q(v)\rangle_{v_z}$ was then determined for the data at each nonzero pressure by subtracting off the zero-pressure background and applying Eq. (2). The results were independent of pressure over the range 50–300 mTorr for the rare gas, independent of sodium density in the range 10^{10} to 8×10^{10} cm^{-3} (corresponding to sodium vapor pressures at temperatures between 95 and 132°C), and independent of the initial laser polarization.

Gas-cell collision experiments such as this one are not "clean" experiments (like crossed-molecular-beam experiments), and consequently care must be taken to assure that the experiment is working as anticipated. The observed good fit of the Maxwell-Boltzmann distribution to the total fluorescence, $F_b(\Delta\nu)$ (see Fig. 2), is excellent evidence that the laser is exciting particles with the expected v_z. (Note that we do not tune far enough off line center to experience trouble from the Lorentz tail of low-velocity atoms.[5]) The rare-gas pressure in this experiment was too low to perturb seriously the excited-state velocity distribution in one radiative lifetime. The Na density was always less than 8×10^{10} cm^{-3} in these experiments and we did not observe any systematic differences in data taken at different Na densities. Radiation trapping, which causes the excitation of non-velocity-selected atoms and artificially lengthens the effective excited-state lifetime [in Eq. (2)] was not a problem at these densities: Even a photon emitted at the center of the cell had $\gtrsim 90\%$ chance of escaping without reabsorption. Furthermore the ratio of the $\frac{1}{2}\rightarrow\frac{3}{2}$ and the $\frac{3}{2}\rightarrow\frac{1}{2}$ transfer rates (which is a sensitive measure of the amount of radiation trapping) was 1.8 ± 0.4 for all our data, in accord with the prediction of

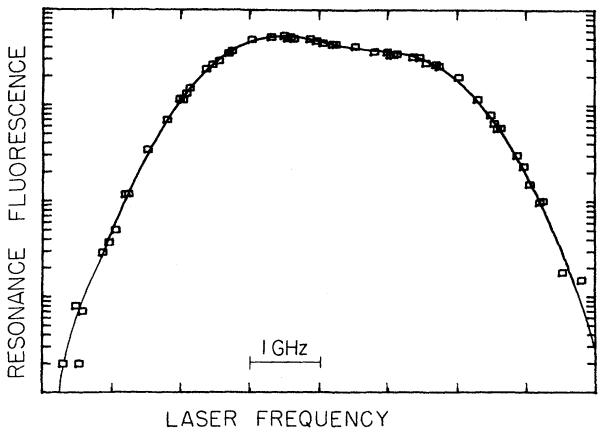

FIG. 2. Resonance fluorescence of the $3p_{1/2}$ line (open symbols) versus laser frequency in a typical run. The solid curve is a Gaussian distribution at the temperature of the cell, taking into account hyperfine structure and resonant absorption of the laser light.

detailed balance (1.91 at 283°C).

The apparatus was carefully tested to make sure that both fluorescence detectors were always operating in a linear regime. A run using He as a target gas (at 50 mTorr) showed a constant ratio $F_t(\Delta\nu)/F_b(\Delta\nu)$ within ± 3% as one would expect from the fact that there is essentially no dependence of $\langle v_{\mathrm{rel}}\rangle$ on v_z in this system because of the high average speed of the He. The presence of such a dependence when using heavier gases, as well as the good fit obtained when the hyperfine structure is convoluted with the cross section of Ref. 4 (which has been independently checked[11] for Na-Ar) is compelling evidence that the VSDS technique is giving reliable results in these systems.

Data for $\langle vQ\rangle$ as a function of average relative velocity (not v_z) are shown in Fig. 3; to obtain this curve we first made a correction for the hyperfine structure, then computed the average relative velocity from $\Delta\nu$ by numerical intergration using Boltzmann distributions for the unselected velocity components in the experiment. We used the same computer code to find the average of the square of the relative velocity (allowing us to calculate $[\langle\Delta v^2\rangle_{v_z}]^{1/2}$ and also to average theoretical cross sections for comparison with our results (these are presented in Figs. 3 and 4)). We believe that systematic errors in the relative velocity dependence are smaller than the observed scatter in the data and that the uncertainty in the absolute scale is ±15%. This scatter is about 5 times larger than one would predict from photon statistics alone and reflects the fact that the total fluorescence and transfer signals were not averaged over identical time intervals so that fluctuations in the laser intensity added noise to the transfer rate.

Qualitatively, our data show that the fine-structure-changing sections, Q, are large and fairly constant over the velocity range studied. The Na-Ar cross section is $\sim 1.25\times10^{-14}$ cm^2 (for $p_{1/2} \rightarrow p_{3/2}$) and falls about 8% with increasing velocity over the range studied in this experiment. The Na-Xe cross section is $\sim 1.05\times10^{-14}$ cm^2 and increases by about 7% over the range studied. The observed difference (between Ar and Xe), both in magnitude and in velocity dependence, contradicts the prediction of Masnou-Seeuws[2] that these cross sections should be independent of the rare gas. The most recent theory, by Pascale and Olson,[4]

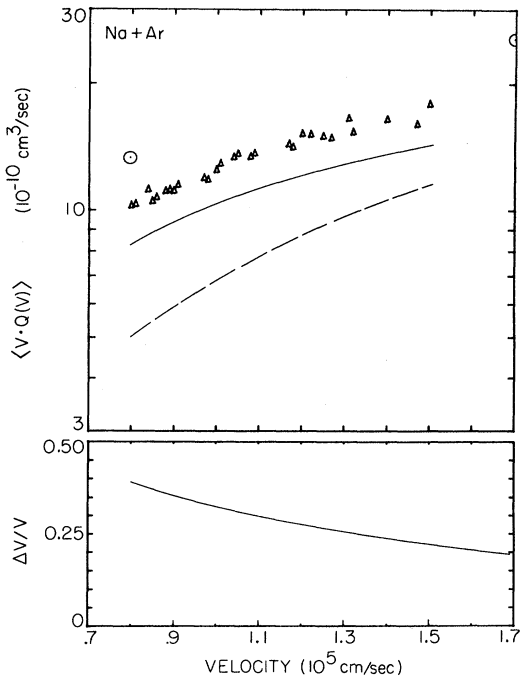

FIG. 3. Experimental rate coefficients for Na($3p_{1/2}$) + Ar → Na($3p_{3/2}$) + Ar versus relative velocity. The solid (dashed) curve was calculated from the theoretical cross section given in Ref. 4 (Ref. 2). A semilog plot has been used to facilitate comparisons of the velocity dependence. The bottom curve is the experimental velocity resolution, $\langle\Delta v^2\rangle^{1/2}/\langle v\rangle$. The open circles are Hanson's data (Ref. 14).

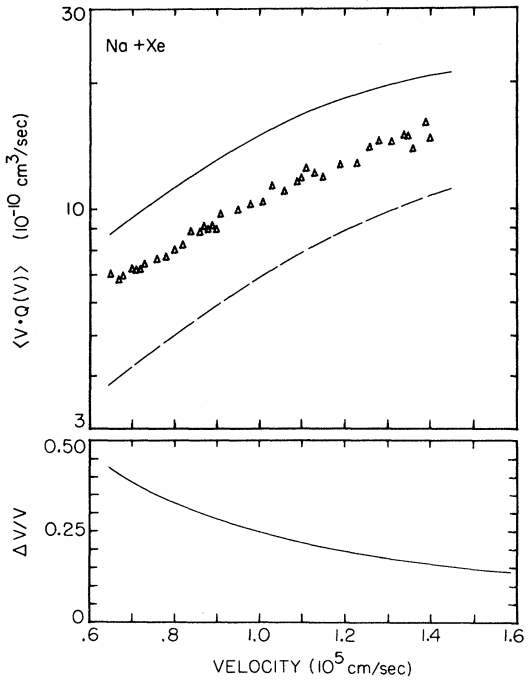

FIG. 4. Rate coefficients for Na($3p_{1/2}$) + Xe → Na($3p_{3/2}$) + Xe (same conventions as Fig. 2).

is in good agreement with the velocity dependence of our results; the discrepancies amount to less than ± 5% and could be entirely experimental in origin. Rate coefficients calculated from Olson's Na-Ar results[3] are not included in Fig. 2 because they are identical to those of Pascale and Olson at low velocity and only 7% above them at the maximum velocity.

In view of the excellent agreement of our measured velocity dependence with Pascale and Olson's calculations, it is surprising to find that the magnitudes of our measured cross sections disagree with these calculations. This discrepancy is most serious for the relative magnitudes of the Na-Ar and Xe cross sections: We find, in accord with Pitre and Krause,[12] that the Ar cross section is larger than the Xe cross section (although they approach equality at higher relative velocity), whereas the calculations show the Xe cross section to be larger (especially at higher velocity). This discrepancy is all the more surprising in view of the relatively good agreement of the $A\Pi$ excited-state potentials used in the calculations with measurements of York, Scheps, and Gallagher.[13]

Our results for Na-Ar are in accord with Hanson's few measurements[14] although he gives no errors and does not estimate his velocity resolution (which is most probably worse than ours). Our results for the absolute cross section are also in excellent accord with Pitre and Krause's non-velocity-selected results[11] if we assume that their excitation lamp had a flat spectrum (so that it did not excite fast or slow atoms preferentially).

Finally, we would like to elaborate on the influence of VSDS-type effects on experiments in which the rate coefficient is measured with conventional light sources. If light having a Gaussian line shape corresponding to the temperature of the interaction region is used, it will preferentially excite slow atoms. For Na-Xe we calculate that this will cause a 16% underestimate of the rate coefficient relative to a source with a flat spectral profile. If the excitation lamp is self-reversed or if the light is appreciably absorbed by atomic vapor prior to reaching the interaction region, then high-velocity atoms will be preferentially excited and much larger errors can occur. These effects will obviously not affect experiments in which there is sufficient background gas to thermalize the velocity distribution of the excited-state species.

We would like to thank W. D. Phillips for helpful discussions on this work.

---

*This work was supported by the U. S. Joint Services Electronics Program Grant No. DAAB07-75-C-1346.

[1]A. Gallagher, Phys. Rev. 172, 88 (1968).

[2]F. Masnou-Seeuws, J. Phys. B 3, 1437 (1970).

[3]R. E. Olson, Chem. Phys. Lett. 33, 250 (1975).

[4]J. Pascale and R. E. Olson, J. Chem. Phys. 64, 3538 (1976).

[5]W. D. Phillips and D. E. Pritchard, Phys. Rev. Lett. 33, 1254 (1974). Preliminary results on Na($3p$) + Rb($5s$) → Na($3s$) + Rb($5p$) are reported by D. E. Pritchard and J. Apt, in *Electronic and Atomic Collisions*, edited by J. S. Risley and R. Geballe (Univ. of Washington Press, Seattle, Wash., 1975), p. 247.

[6]A. T. Mattick, A. Sanchez, N. A. Kurnit, and A. Javan, Appl. Phys. Lett. 23, 675 (1973).

[7]T. W. Meyer and C. K. Rhodes, Phys. Rev. Lett. 32, 637 (1974).

[8]S. M. Freund, J. W. L. Johns, A. R. W. McKellar, and T. Oka, J. Chem. Phys. 59, 3445 (1973).

[9]M. Elbel, H. Huhnermann, Th. Meier, and W. B. Schneider, to be published.

[10]R. A. Bernheim, *Optical Pumping: An Introduction* (Benjamin, New York, 1965).

[11]W. D. Phillips's preliminary measurements of Na-Ar in a crossed-beams machine confirm the relative velocity dependence of Ref. 4 (private communication).

[12]The results of B. Pitre and L. Krause, Can. J. Phys. 45, 2671 (1967), are consistent with our lowest velocity data within 5%.

[13]G. York, R. Scheps, and A. Gallagher, J. Chem. Phys. 63, 1052 (1975).

[14]H. G. Hanson, J. Chem. Phys. 27, 491 (1957).