Crossed-Beam Determination of Na–Rare-Gas Fine-Structure-State–Changing Cross Sections*

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We report first measurements of the velocity dependence of an alkali–rare-gas fine-structure-state–changing collision with adequate range and resolution to reveal a peak in the cross section. The method uses crossed atomic beams and selective laser excitation. Results are presented for Na colliding with Ne, Ar, and Kr. The results for Na-Ar are in good agreement with theory, while those for Na-Ne and Na-Kr are in serious disagreement.

Fine-structure-state–changing (FSSC) collisions of alkali atoms with rare-gas atoms represent a model process for the study of inelastic collisions in an electronically excited system. Extensive calculations of excited alkali–rare-gas potentials have been carried out,[1,2] and the results have been used by a number of workers to calculate velocity-dependent FSSC collision cross sections.[3-6] Although experimental studies of FSSC collisions have a long history,[7] comparisons of the predicted velocity dependence of the cross sections with experiment have only recently become possible. We present here the first measurements of a FSSC cross section with sufficient velocity range and resolution to reveal the general features predicted by theory, including the velocity at which the cross section peaks.

Previous work includes gas-cell measurements by Gallagher[8] on the temperature dependence of FSSC collisions for Rb and Cs. For these atoms, the fine-structure separation ΔE is so big that for thermal velocities the Massey parameter, $\xi = \Delta E\tau/\hbar$ (where τ is the effective collision time), is large. The cross section, which has a maximum when ξ is of order unity, is observed to increase rapidly with velocity. Gallagher's experiments took advantage of this rapid increase to achieve a velocity resolution of 30–40%, but the method does not permit observation of $\sigma_{\mathrm{FSSC}}(v)$ with good resolution over a range which includes the peak cross section.

Anderson *et al.*[9] have used atomic beams to study $\sigma_{\mathrm{FSSC}}(v)$ for K-He collisions with 20–30% velocity resolution. The use of K, with $\Delta E = 58$ cm^{-1}, again resulted in a Massey parameter so large that only a linear increase of σ_{FSSC} with v was observed. Apt and Pritchard[10] have applied the technique of velocity selection by Doppler shift[11] (VSDS) to study Na-Ar and Na-Xe FSSC collisions in a gas cell. While the experiment covered a velocity range which was theoretically predicted to include the peak cross section, the resolution, 30–80%, only permitted observation of a monotonic increase (Xe) or decrease (Ar) in the cross section.

We have combined the techniques of crossed atomic beams and VSDS to measure $\sigma_{\mathrm{FSSC}}(v)$ for the process

$$\mathrm{Na}(3P_{3/2}) + X \rightarrow \mathrm{Na}(3P_{1/2}) + X + \Delta E, \qquad (1)$$

where X represents Ne, Ar, or Kr. The velocity range was $(0.4\text{–}2.6)\times10^5$ cm/sec, and the velocity resolution was between 5% and 15%. Isolation of the transfer and resonance signals, separated by $\Delta E = 17$ cm^{-1}, was achieved by use of a double monochromator and careful optical design. The technique yields good counting rates and should be applicable to a wide range of systems.

The experiment uses a collimated Na beam, a free rare-gas beam, and a laser beam which intersect in an interaction region. The rare-gas beam is operated in the regime of supersonic flow; its velocity spread was estimated to be less than 10% on the basis of measurements by other workers with similar operating conditions[12,13] A cw single-mode tunable dye laser provides the laser beam which intersects the Na beam at an angle of about 5° and excites the transition $3S_{1/2} \rightarrow 3P_{3/2}$. The velocity of atoms which are excited is selected by varying the laser frequency in a manner similar to the VSDS technique. The selective excitation process has been studied in some detail by Hertel *et al.*[14]

The collision energy range can be extended by varying the angle between the Na and rare-gas beams. To obtain data in this manner the rare-gas beam is rotated horizontally while the laser is directed vertically along the rotation axis. Because the velocity resolution with this method was only about 40%, the data obtained are not in-

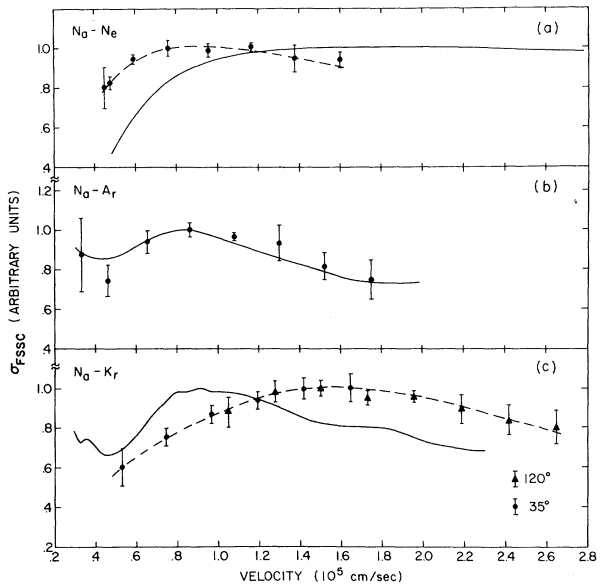

FIG. 1. σ_{FSSC} vs relative velocity. Solid curves are theoretical (Ref. 6); dashed curves are estimated fits to experimental points.

cluded below. With the addition of a velocity selector the rotation method would yield much higher resolution.

σ_{FSSC} is determined from measurement of the fluorescence. Resonance fluorescence at the $3P_{3/2} \rightarrow 3S_{1/2}$ wavelength provides a measure of the number of excited Na atoms in the interaction region, while the transfer fluorescence at the $3P_{1/2} \rightarrow 3S_{1/2}$ wavelength revelas the number of atoms which have undergone the FSSC reaction, Eq. (1). The ratio of transfer fluorescence to resonance fluorescence is proportional to the FSSC collision rate; dividing this rate by the collision velocity yields relative values of $\sigma_{FSSC}(v)$. We have not attempted to measure absolute cross sections, which are better measured by gas-cell techniques.[7,8,10]

Figure 1(a) shows results for Na-Ne measurements taken using laser Doppler velocity selection with the atomic beams intersecting at 35°. The experimental points, normalized to the maximum cross section, are compared with the theoretical prediction of Pascale and Olson,[6] similarly normalized. The uncertainties represent the scatter between data taken in different runs. Since the theoretical curves have been calculated for the process $3P_{1/2} \rightarrow 3P_{3/2}$, we have used detailed balance to provide the relation

$$\sigma_{j \rightarrow j'}(E) = \sigma_{j' \rightarrow j}(E')(E'/E) g_{j'}/g_j \qquad (2)$$

to obtain $\sigma_{3/2 \rightarrow 1/2}(E)$ from $\sigma_{1/2 \rightarrow 3/2}(E')$ where E is the initial center-of-mass energy and $E' = E + \Delta E$. g_j is the degeneracy of the j state.

From Fig. 1(a) it is clear that while the theoretical cross section peaks at about 2×10^5 cm/sec relative velocity, the data peak near 1×10^5 cm/sec. This conclusion is corroborated by the lower-resolution data taken by the beam-rotation method (not shown) which clearly show that the cross section decreases at velocities above 1×10^5 cm/sec.

Figure 1(b) shows Na-Ar cross-section curves compared with the Pascale-Olson theory. Agreement is good, and the peak cross section is accurately located. Detailed comparison at the lowest and highest velocities is difficult because of poor statistics, but it is clear the the general shape of the curve is correctly predicted by theory. The relatively large uncertainty at low velocities arises from corrections for excitation of fast atoms from the $3S_{1/2}(F=1)$ state in addition to slow atoms from the $3S_{1/2}(F=2)$. Data taken by the rotation method (not shown) agree with the theory to within the experimental errors of about 3%.

Figure 1(c) shows Doppler-selected data for Na-Kr collisions with the beams at 35° and 120°. The data for the two different angles have been separately normalized to the peak cross section at $v \cong 1.5 \times 10^5$ cm/sec and are compared with the normalized Pascale-Olson prediction. There is a clear disagreement, but in this case the theory is seen to predict a peak at too *low* a velocity, in contrast to the case for Na-Ne.

Our conclusion is that the velocity dependence of Na-Ar FSSC cross section is accurately predicted by theory while Na-Ne and Na-Kr calculations make a serious error in the location of the peak cross section.

When our results are suitably averaged over the collision velocity distribution for the VSDS experiment, we obtain collision rates which are in good agreement with those measured by Apt and Pritchard for Na-Ar[10] and Na-Ne.[15]

Pascale and Olson[6] have related the general features of the cross-section curves to the behavior of $\Delta V = V(\Sigma) - V(\Pi)$, the separation between the quasimolecular Na-X potentials arising from the ^2P state of Na in the absence of spin-orbit coupling. They suggest, for example, that behavior such as we observe in σ_{FSSC} (Na-Ne) correlates with a larger slope of ΔV than assumed in the region where $|\Delta V| \approx \Delta E$ (around 15 a.u.). Interpretation of the discrepancy between theory

and experiment for Na-Kr is complicated by the fact that theory predicts that there are two regions around 13 and 15 a.u. for which $|\Delta V| \approx \Delta E$, and that σ_{FSSC} has two peaks, one at too low a velocity for observation with our present techniques. Calculations of $\sigma_{FSSC}(v)$ for Na-Kr using other potentials are needed to identify the cause of the discrepancy.

Carter *et al.*[16] have found disagreement between the results of elastic scattering experiments with Ne and excited Na and the predictions based on the Pascale-Vandeplanque potentials. They observed a well depth for the Π potential 20 times greater than predicted. The experiment was sensitive to internuclear separations smaller than those important for FSSC collisions; taken together with our results, the experimental picture suggests that the calculated Na-Ne potentials may be in error over a wide range of internuclear separation.

Although our collision measurements agree with calculations based on the Pascale-Vandeplanque potentials for Na-Ar, spectroscopic measurements on the $A-X$ transition in Na-Ar by York, Scheps, and Gallagher[17] reveal that the Π potential well depth is about twice that predicted. In contrast, for the case of Na-Kr, the York-Scheps-Gallagher measurements are in better agreement with the Pascale-Vandeplanque potential, but our FSSC measurements disagree sharply with theory. The spectroscopic measurements are sensitive to the potential at smaller distances than are FSSC collisions; and it is apparent that agreement between theoretical and spectroscopically observed potentials is no guarantee of theoretical accuracy in the difference potentials at larger distances where inelastic collisions occur.

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Note added.—R. P. Saxon and R. E. Olson have communicated to us new theoretical results for $\sigma_{FSSC}(v)$ based on an *ab initio* configuration-interaction calculation of the potential. Their results are in excellent agreement with our data for Na-Ar.

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[1]W. E. Baylis, J. Chem. Phys. 51, 2665 (1969).

[2]J. Pascale and J. Vandeplanque, J. Chem. Phys. 60, 2278 (1974).

[3]R. H. G. Reid and A. Dalgarno, Phys. Rev. Lett. 22, 1029 (1969).

[4]R. H. G. Reid, J. Phys. B 6, 2018 (1973).

[5]R. E. Olson, Chem. Phys. Lett. 32, 250 (1975).

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

[7]A review of the subject is given by P. L. Lijnse, Fysisch Laboratorium, Rijksuniversiteit, Report No. 398, 1972 (unpublished). Early experimental methods and results are reviewed by L. Krause, Appl. Opt. 5, 1375 (1966).

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

[9]R. W. Anderson, T. P. Goddard, C. Porravand, and J. Warner, J. Chem. Phys. 64, 4037 (1976).

[10]J. Apt. and D. E. Pritchard, Phys. Rev. Lett. 37, 91 (1976).

[11]W. D. Phillips and D. Pritchard, Phys. Rev. Lett. 33, 1254 (1974).

[12]J. M. Parson, P. E. Siska, and Y. T. Lee, J. Chem. Phys. 56, 1511 (1972).

[13]P. E. Siska, J. M. Parson, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. 55, 5762 (1971).

[14]J. V. Hertel, H. Hofmann, K. A. Rost, and S. Azankadeh, J. Phys. E 8, 1023 (1975).

[15]J. Apt and D. E. Pritchard, to be published.

[16]G. M. Carter, D. E. Pritchard, M. Kaplan, and T. W. Ducas, Phys. Rev. Lett. 35, 1144 (1975).

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