Differential Scattering of Na $3S_{1/2}$ and $3P_{3/2}$ from Ne: Determination of Ground- and Excited-State Potentials for NaNe†

Gary M. Carter, David E. Pritchard, Martin Kaplan, and Theodore W. Ducas
Department of Physics and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 24 July 1975)

We report high-resolution measurements of the differential cross section for scattering Na in its $3S_{1/2}$ and $3P_{3/2}$ states from Ne. A new scheme is used to maintain a high fraction (~20%) of an atomic beam of Na in the excited state for many radiative lifetimes using a single-mode cw dye laser. The differential cross sections are interpreted to yield interatomic potential curves for both the $X\Sigma$ and $A\Pi$ states of the NaNe molecule which seriously disagree with recent pseudopotential calculations.

In this Letter we report high-resolution measurements of the differential scattering cross sections for sodium in both its $3S_{1/2}$ and $3P_{3/2}$ states from ground-state neon. These measurements demonstrate for the first time the feasibility of high-resolution atomic-scattering studies using primary beams of electronically excited atoms. (A cw dye laser was used to maintain a significant portion of the atoms in the primary sodium beam in the excited state.) We interpret the cross sections to obtain information about the ground- and excited-state interatomic potentials for NaNe. The results presented here are the first measurements of the differential scattering of atoms on states which are optically accessible from the ground state.[1]

The principal problem in this experiment is to maintain a significant fraction of the primary beam atoms in the excited state as they pass through the scattering region (which takes ~100 radiative lifetimes). This requires a scheme to prevent the atoms from decaying to an F, m_F hyperfine component of the ground state from which the single-frequency laser[2] cannot re-excite them. We have devised a scheme which permits the laser to excite all F, m_F levels of the ground state[3]: The Doppler shift is utilized to produce a frequency spectrum which can excite atoms in both hyperfine components of the $3s$ state, and a small magnetic field is used to mix the magnetic sublevels of both hyperfine components in a time short compared with the time it takes for the population to accumulate in one of them. To realize this scheme experimentally, laser light whose frequency lies midway between the frequencies required to excite the two hyperfine components is bounced back and forth at an angle with respect to the primary atomic beam. Photons with a component of velocity along (opposite to) the atomic beam are shifted to the red (blue) and pump the upper (lower) hfs component. The scheme is described in detail in another paper.[4]

This experiment was conducted in a conventional atomic-beam-scattering machine.[5] Na atoms from a source oven passed through a focusing magnet to increase their intensity in the scattering region, and the scattered atoms (at laboratory angle θ_l) passed through a mechanical velocity selector on their way to a hot-wire detector. Gas in the target chamber was at room temperature. Measurements of the detector counting rate were made at each angle both with the laser light on and with it off. The differential cross section for scattering Na($3s$) from Ne, $\sigma_X(\theta_l)$, was determined from the light-off measurements. The difference between light-on and light-off measurements (typically a 10% difference) was used to determine $\sigma^*(\theta_l)-\sigma_X(\theta_l)$. It was not possible to use these measurements to determine $\sigma^*(\theta)$ directly because the excited-state fraction of the beam could not be determined accurately. Furthermore atoms from a restricted region of velocity and space were preferentially excited. Thus the excited-state scattering data had better velocity resolution than the ground-state data, but had to be reduced with use of a different angular dependence for the scattering volume.

Before discussing the analysis of the excited-state data we first consider the analysis of the ground-state scattering data. The differential cross section for the scattering of the ground-state sodium from neon, $\sigma_X(\theta)$, is shown in Fig. 1, multiplied by $\theta^{4/3}\sin\theta$. The data have been transformed to the center-of-mass coordinate system, but no allowance has been made for the averaging over these variables caused by the finite velocity resolution (10%) of the apparatus and by the motion of the target gas. The cross sec-

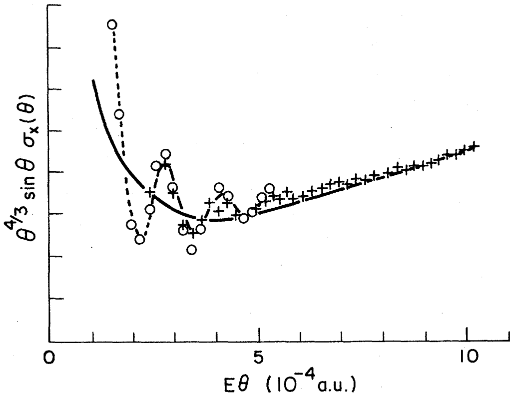

FIG. 1. Differential cross section for scattering of ground-state Na from Ne. Solid line is average cross section calculated from an MSV potential using $r_{mX} = 9.0a_0$ and $\epsilon = 12$ cm^{-1}, and normalized to agree with the data in the region beyond 6×10^{-4} a.u. The dotted (dashed) line emphasizes the rapid oscillations in the experimental points ○ (+) taken with a 2 (5) mrad resolution. $E = 5.0\times10^{-3}$ a.u.

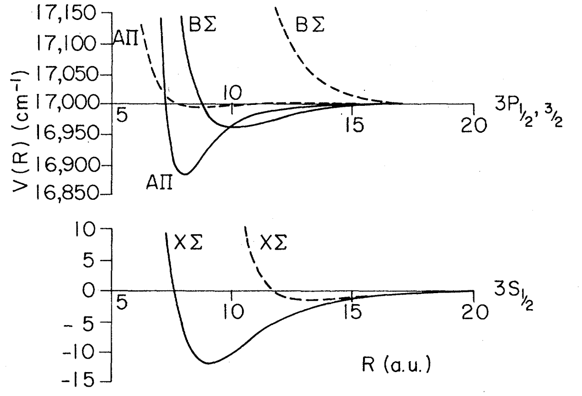

FIG. 2. Interatomic potentials determined from this work (solid lines) compared with theoretical calculations of Pascal and Vandeplanque (dashed lines).

tion displays rapid oscillations, a sharp increase as $\theta \to 0$, and a monotonic rise at moderate angles. Such a pattern is characteristic of scattering from weakly attractive interatomic potentials.[6] The period of the oscillations (which are similar to the oscillations of diffraction scattering from a disk) gives an accurate measurement of the size of the potential in terms of the de Broglie wavelength of the scattering system. The shape of the small-angle falloff of the cross section depends on the well depth. Fits to the measured ground-state differential cross section were made by assuming a Morse potential form for the potential near the minimum, and adjusting the curvature of this potential so that it could be joined smoothly onto a van der Waals potential[7] at long range by use of a spline function. (This is called an MSV potential form.) The results for the well depth and position of the ground-state potential are $\epsilon_X = 11^{+3}_{-5}$ cm^{-1} and $r_{mX} = 9.1(4)a_0$ (which matches the positions of all rapid oscillations within 0.2×10^{-4} a.u.).

We know of no previous measurements of the ground-state differential cross section of Na and Ne; however our results are consistent with the value $\epsilon_X r_{mX}/a_0 = 86(9)$ cm^{-1} obtained by Düren, Frick, and Schlier[8] from measurements of the total cross section of Na and Ne. They are also quite similar to the values obtained ($\epsilon_X = 9.0$ cm^{-1} and $r_{mX} = 9.6a_0$) by Dehmer and Wharton[9] from total-cross-section measurements on the chemically similar system LiNe.

The analysis of the cross section $\sigma^* - \sigma_X$ is much less straightforward than the preceding analysis of σ_X because the system Na(3p) + Ne can collide along either of two potential curves (corresponding to the $A\Pi$ and $B\Sigma$ states; see Fig. 2), and because of complications arising from the spin-orbit interaction. If the system scattered on the adiabatic potential curves shown in Fig. 2, it would be possible to isolate scattering from the $A\Pi$ curve by scattering $P_{1/2}$ atoms. However, there are two reasons for believing that the system Na(3p) + Ne scatters diabatically at the collision energies studied here: The first is the large magnitude (~ 80 Å^2) of the cross section for changing the fine-structure state of the Na in the collision,[10] and the second is that our preliminary results for the differential scattering of $P_{1/2}$ Na atoms (not shown in this paper) are essentially identical to the result for $P_{3/2}$ atoms (except that they have more noise because we were able to excite only about $\frac{1}{2}$ as many atoms to the $P_{1/2}$ state as to the $P_{3/2}$ state). Consequently, we believe that the fractions of $A\Pi$ and $B\Sigma$ involved in the scattering of $P_{3/2}$ atoms may be determined statistically, i.e., that

$$\sigma^*(\theta) = \tfrac{2}{3}\sigma_A(\theta) + \tfrac{1}{3}\sigma_B(\theta), \qquad (1)$$

where σ_A (σ_B) is the differential cross section for scattering from the $A\Pi$ ($B\Sigma$) potential. This expression also requires that there be no alignment of the electronic angular momentum along the axis of the quasimolecule formed during the collision; this was checked at several angles by varying the direction and strength of the magnetic field used to mix the m sublevels. This

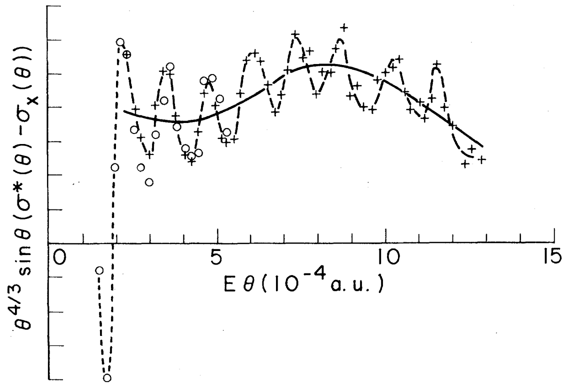

FIG. 3. Differential cross section $\sigma^*-\sigma_X$. The solid line is the average cross section computed with use of MSV potentials with $r_m=(9.0, 8.0, 10.0)a_0$ and $\epsilon=12, 120, 40$ cm^{-1} for the $X\Sigma$, $A\Pi$, and $B\Sigma$ potentials, respectively. The dotted (dashed) line emphasizes the rapid oscillations in the experimental points ○ (+) taken with a 2 (5) mrad resolution. $E=5.0\times10^{-3}$ a.u.

produced no change in the scattering signal although the field significantly altered the excited-state alignment.

Measurements of $\sigma^*(\theta)-\sigma_X(\theta)$ for Na in the $3P_{3/2}$ state are shown in Fig. 3. Noteworthy features of these data include the broad maximum centered around $E\theta=8\times10^{-4}$ a.u., the existence of rapid oscillations throughout the entire range of the data, and the large amplitude of the rapid oscillations at the smallest angles. (Note also that $\sigma^*-\sigma_X$ is negative near $E\theta=2\times10^{-4}$ a.u.) The persistence of rapid oscillation out to $E\theta=12\times10^{-4}$ a.u. indicates scattering from a potential whose well depth must be deeper than 60 cm^{-1}. A potential this deep must produce rainbow structure within the angular range observed, and we identify the broad maximum as this feature. (We attribute some of the width of this peak to averaging caused by the motion of the target gas.)

We have attempted to fit both the average shape and the positions of the rapid oscillations of the cross section $\sigma^*-\sigma_X$ by using MSV potential forms for both the $A\Pi$ and the $B\Sigma$ excited-state potentials. The excited-state van der Waals coefficient, C_6, was taken from Baylis's calculations[11] and the ratio C_8/C_6 was arbitrarily assumed to be the same as for the ground state. The fit to $\sigma^*-\sigma_X$ for $E\theta$ beyond 6×10^{-4} is sensitive principally to the $A\Pi$ potential and yields $\epsilon_A=120(15)$ cm^{-1} and $r_{mA}=8.0(3)a_0$ (which matches the positions of all rapid oscillations to within 0.2×10^{-4} a.u.).

The fit to $\sigma^*-\sigma_X$ in the region $0<E\theta<6\times10^{-4}$ depends sensitively on all three potentials. In addition, small deflections produced by spin-orbit forces [which are neglected by our Eq. (1)] may affect both the average cross section and the amplitude of the rapid oscillations. Thus little significance should be attached to the values obtained for the B-state parameters ($\epsilon_B=40$ cm^{-1} and $r_{mB}=10.0a_0$) which were used to obtain the fit shown in Fig. 3.

Two similar pseudopotential calculations have been made of alkali–rare-gas interatomic potentials.[11,12] These calculations give quite similar potentials (well depths for NaNe X, A, and B states are 1.8, 12, and 0.3 cm^{-1} and 1.8, 6, and 1.5 cm^{-1}, respectively). We have compared the potentials which we used to fit our data with only the Pascale-Vandeplanque potentials since their basis set was somewhat larger (and hence their potentials should be more reliable). A major portion of the large discrepancy between these calculations and our results probably can be removed within the spirit of these calculations by reducing the radius of the rare gas used in the calculations to fit our ground-state potential-well depth. It seems unlikely that this will bring the predicted ratio of ϵ_A/ϵ_X into agreement with our measurements, however. It is interesting to note that experimental measurements of ϵ_A[13] and ϵ_X[14] in NaAr yield a ratio $\epsilon_A/\epsilon_X=13$, nearly the same ratio obtained in the present experiment.

The techniques developed and demonstrated in this experiment for studying the differential cross sections of laser-excited atoms have many applications besides elastic-scattering studies like these. For example, the transfer of the electronic energy added by the laser to the internal degrees of freedom of a molecular target could be studied by a velocity analysis of the scattered atoms. It is also likely that excited-state atoms will prove to be highly reactive species whose chemistry may be studied profitably by molecular-beam-scattering techniques. In short, the laser offers an excellent way selectively to add energy (and possibly angular momentum) to thermal-energy collisions; our technique should permit the investigation of processes which are energetically forbidden in collisions between unexcited partners.

We would like to thank N. Saleh for help in taking the data.

---

†Work supported by National Science Foundation Grant No. MPS75-15421.

[1] High-resolution experiments using metastable-atom beams are fairly common—see *Electronic and Atomic Collisions*, edited by J. S. Risley and R. Geballe (Univ. of Washington Press, Seattle, Wash., 1975), pp. 433–445. Optically excited Na has been used as a target for electron scattering.

[2] A Spectra Physics Model No. 580 dye-laser system gave approximately 70 mW single mode at 5890 Å.

[3] R. Schieder, H. Walther, and L. Woste, Opt. Commun. 5, 337 (1975), have demonstrated a scheme to pump the $F=3$ hfs component of the $P_{3/2}$ level which can decay only to the $F=2$ level of the ground state.

[4] G. M. Carter, D. E. Pritchard, and T. W. Ducas, Appl. Phys. Lett. 27, 498 (1975).

[5] Our machine is described by G. M. Carter and D. E. Pritchard, J. Chem. Phys. 62, 927 (1975).

[6] H. Pauly and J. P. Toennies, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1965), Vol. I, p. 201.

[7] The (attractive) coefficients for sixth and eighth powers were taken from A. Dalgarno and W. D. Davison, Mol. Phys. 13, 479 (1967), and from W. D. Davison, J. Phys. B: At. Mol. Phys. 1, 139 (1968), respectively.

[8] R. Düren, A. Frick, and Ch. Schlier, J. Phys. B: At. Mol. Phys. 5, 1744 (1972).

[9] P. Dehmer and L. Wharton, J. Chem. Phys. 57, 4821 (1972).

[10] Na-Ne fine-structure–changing collisions should have cross sections similar to those for Na+He; see M. Elbel, A. Koch, and W. Schneider, Z. Phys. 255, 14 (1972).

[11] W. E. Baylis, J. Chem. Phys. 51, 2665 (1969), and Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Report No. 100 (unpublished).

[12] J. Pascal and J. Vandeplanque, J. Chem. Phys. 60, 2278 (1974).

[13] We thank Alan Gallagher for copies of his unpublished determinations of alkali–rare-gas excited-state potentials for the systems NaAr, NaKr, and NaXe. These potentials were determined by an analysis of continuum radiation using techniques described by D. L. Drummond and A. Gallagher, J. Chem. Phys. 60, 3426 (1974), and by R. E. M. Hedges, D. L. Drummond, and A. Gallagher, Phys. Rev. A 6, 1519 (1972).

[14] R. Düren, G. P. Raabe, and Ch. Schlier, Z. Phys. 214, 410 (1968).

Derivation of Dispersion Relations for Atomic Scattering Processes*

F. W. Byron, Jr.
Department of Physics, University of Massachusetts, Amherst, Massachusetts 01002

and

F. J. de Heer
Fundamenteel Onderzoek der Materie-Instituut voor Atoom- en Molecuulfysica, Amsterdam, The Netherlands

and

Charles J. Joachain
Physique Théorique, Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium, and
Institut de Physique Corpusculaire, Université de Louvain, Louvain-la-Neuve, Belgium

(Received 23 June 1975)

We point out that it now appears very likely that because of the properties of the exchange amplitude the customary forward dispersion relations do not hold for electron-atom elastic scattering.

In this note we wish to point out that recent experimental progress makes it seem very likely that the customary forward dispersion relations do not hold for electron-atom elastic scattering.

Let us begin by assuming that we are dealing with nonrelativistic elastic scattering of electrons by noble gases where the scattering amplitude can be written as

$$f(E,\theta)=f^d(E,\theta)-g(E,\theta), \tag{1}$$

f^d being the direct amplitude and g being the exchange amplitude. [We shall also use the first Born approximation to f^d and g, which we shall denote respectively by $f_{B1}{}^d$ and g_{B1}; all quantities will be expressed in atomic units (a.u.).] If we restrict our attention to forward scattering and assume that, as in potential scattering, $f(E,0)$ [denoted henceforth as $f(E)$] is analytic in the complex E plane cut along the positive real axis, then we may write

$$2\pi i\, f(E)=\oint_C \frac{f(E')}{E'-E}\,dE'. \tag{2}$$

Here C is the well-known contour in the cut plane