curves for small values of n have been omitted, but will be included in a subsequent publication.[11] In the regions where the triplet and singlet channels cross there is a slight mixing of the channels, which gives rise to the multiphoton ionization signals seen from the triplet states (Table I). The strong interaction between the $4snd\,^1D_2$, $3d5s\,^1D_2$, and $3d^2\,^1D_2$ configurations is clearly seen in the substantial deviation of the channels from the horizontal or vertical lines which would be predicted for Ca in the absence of such interactions. It is obvious that assigning unmixed configurations to particular peaks is highly suspect for $^1D_2$ states. In fact, the multichannel analysis[11] shows that none of the newly observed $^1D_2$ states contains more than a few percent admixture of $3d5s$ or $3d^2$. By contrast, the quantum defects for the $4sns\,^1S_0$ states (Table I) show no evidence of perturbation by the (as yet unobserved) $3d^2\,^1S_0$ state.

We gratefully acknowledge useful discussions with Dr. P. P. Sorokin and the technical assistance of Mr. L. H. Manganaro.

---

*Supported in part by the U. S. Army Research Office.

[1] F. Biraben, B. Cagnac, and G. Grynberg, Phys. Rev. Lett. 32, 643 (1974); M. D. Levenson and N. Bloembergen, Phys. Rev. Lett. 32, 645 (1974).

[2] D. Popescu, C. B. Collins, B. W. Johnson, and I. Popescu, Phys. Rev. A 9, 1182 (1974).

[3] R. M. Hochstrasser, H. N. Sung, and J. E. Wessel, J. Chem. Phys. Lett. 24, 7 (1974).

[4] P. M. Johnson, J. Chem. Phys. 62, 4562 (1975).

[5] G. Risberg, Ark. Fys. 37, 231 (1968).

[6] C. M. Brown, S. G. Tilford, and M. L. Ginter, J. Opt. Soc. Am. 63, 1454 (1973).

[7] T. W. Hänsch, Appl. Opt. 11, 895 (1972).

[8] T. W. Ducas, M. G. Littman, R. R. Freeman, and D. Kleppner, Phys. Rev. Lett. 35, 366 (1975).

[9] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), Chap. 11.

[10] U. Fano, J. Opt. Soc. Am. 65, 979 (1975), and refercences cited therein.

[11] J. A. Armstrong, P. Esherick, and J. J. Wynne, to be published.

Optical Potential for He(2^1S) + Ar from High-Resolution Differential Scattering Experiments

B. Brutschy, H. Haberland, H. Morgner, and K. Schmidt
Fakultät für Physik der Universität Freiburg, 78 Freiburg im Breisgau, West Germany

(Received 20 January 1976)

The real and imaginary parts of the interaction potential of metastable He(2^1S) with argon have been accurately determined from high-resolution differential scattering experiments. The real part of the potential shows an unexpected structure with two minima, while the imaginary part is monotonic, but cannot be expressed by a single exponential.

If a metastable helium atom (He*) collides with a ground-state argon atom it can either be scattered elastically or it can ionize the argon because its excitation energy is more than 4 eV higher than the ionization potential of argon. This inelastic process, called Penning ionization, has been extensively studied in recent years.[1] The ionization causes a loss of flux from the incident beam. When inelastic channels are open a scattering process can be phenomenologically described by a complex potential $W(R)=V(R)-i\Gamma(R)/2$, where $\Gamma(R)$ is usually called the width of the potential. Complex or optical potentials which have been used extensively in nuclear physics[2] have also been used in the analyses of molecular-beam experiments with metastable helium[3,4] and with chemically reactive molecules.[5] If the optical potential is defined rigorously it becomes energy dependent and nonlocal.[2,5] In the case of scattering metastable helium from atoms, a local Born-Oppenheimer–type of approximation will probably be rather good, because the loss from the incoming channel is due to an electronic transition which is very fast compared to the heavy-particle motion.

A large number of experiments have been performed to determine some of the properties of the He*-Ar system. Measurements have been made of the energy dependence of the total elastic cross section, of quenching and ionization rate constants and cross sections, and of the velocity dependence of the Penning electron energy and angular distributions.[1] The angular distributions of the resulting Ar$^+$ have also been measured.[6] The theory has been developed mainly by Nakamura[7] and Miller.[8]

We have studied in a high-resolution experiment the elastic scattering of metastable helium ($1s2s, 2^1S$) from argon and have been able to determine an accurate optical interaction potential. The resolution of the two earlier differential scattering experiments[3,4] was not sufficient to allow an unambiguous determination of the potential. The details of the present experiment are similar to those described in Ref. 4; however, significant improvements have been made in both the velocity and angular resolution. Atoms in a free jet of helium are excited by electron impact to the two metastable states. The singlet state can be quenched optically.[1] The beam is crossed by a second free jet of argon atoms and the number of scattered metastables is counted. For each angle data taken with and without the quench lamp are automatically subtracted and normalized to the intensity of an out-of-plane monitor detector. All experimental details will be described more fully elsewhere.[9]

The measured differential cross sections are shown in Fig. 1 for three different center-of-mass energies. The small-angle oscillations which are very sensitive to the location of the repulsive wall are clearly resolved. Only the angular distribution at 21 meV does not show the pronounced maximum which shifts to smaller angles with increasing energy. Beyond this maximum the intensity drops rapidly. The data become noisy because they consist of the small differences (~ 0.5 counts/sec) of two larger numbers.

No inversion procedure exists for complex potentials. Therefore the differential cross section was calculated from assumed complex potentials, using a complex Numerov integration method[10] for the Schrödinger equation. A Morse-type interaction potential was unable to produce the observed large variations in the angular distributions. Also the peak in the angular distribution could not be explained by a mirrorlike reflection from a steeply rising imaginary potential. A good fit was obtained using a potential with two minima separated by a sharp maximum as shown in Fig. 2. The rainbow scattering[11] from this maximum causes the observed peak in the angular distributions. The imaginary part of the potential is purely monotonic. The calculated differ-

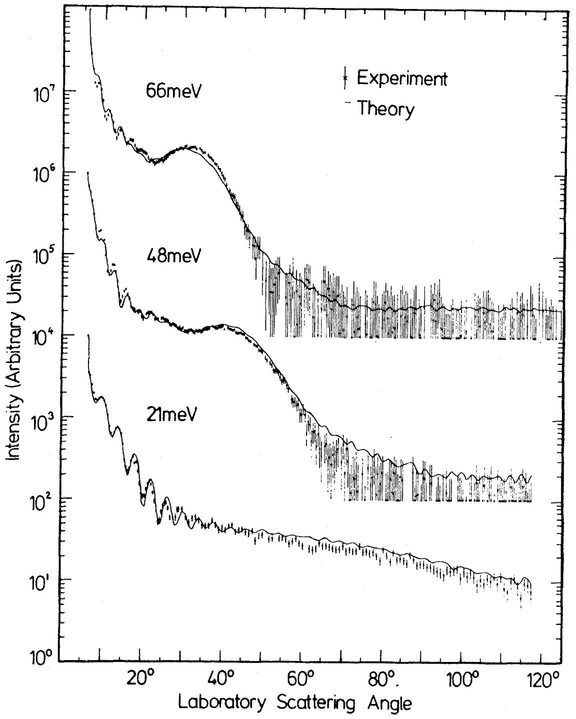

FIG. 1. Differential cross sections for He(2^1S) + Ar in the lab system for three different center-of-mass energies. The theoretical result calculated from the potential shown in Fig. 2 is given by the solid line. The peak in the differential cross section is due to rainbow scattering from the intermediate maximum in the interaction potential. For 66 and 48 meV some of the error bars have been terminated for clarity of display.

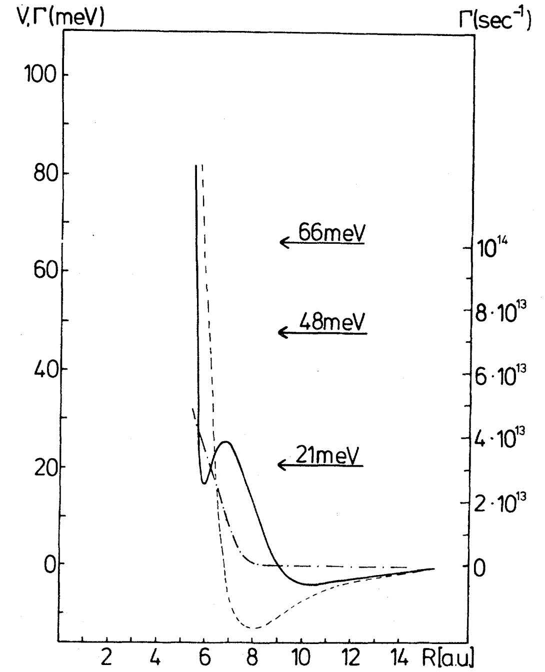

FIG. 2. Real (——) and imaginary (-•-•) part of the interaction potential used to calculate the solid curve in Fig. 1. The three energies for which the experiments have been performed are indicated. The dashed line shows the real part of the potential proposed by Olson.

ential cross sections appropriately transformed and averaged are compared to the experimental data in Fig. 1.

Most of the parameters of the potential were determined by the nonlinear iterative least-squares procedure due to Marquardt.[12,13] Using the usual method[13] of constructing piecewise analytical potentials and joining them with spline functions caused the least-squares program to diverge if more than some well-behaved Morse parameters were varied. Therefore the overall shape of the potential was fixed as the sum of two Morse potentials and two of its parameters were varied for fine tuning the potential in the region of the repulsive wall and outside the intermediate maximum. The double Morse functions were asymptotically coupled by a cubic spline interpolation to a R^{-6} potential, whose Van der Waals constant had been previously calculated.[14] The potential is given below (energies are in electron volts and distances in atomic units):

$$V(R)=\sum_{i=1}^{2} D_i E_i(E-2),\quad E_i=\exp[\beta_i(1-X/R_i)],\quad D_1=0.00347,\quad R_1=10.703,\quad \beta_1=5.44,$$

$$D_2=0.549,\quad R_2=5.33;$$

$$\beta_2=\begin{cases} 8.23\{0.668+0.332\exp[-2(R-5.63)^2]\}, & R\leqslant 5.63,\\ 8.23, & 5.63\leqslant R\leqslant 1.2R_1;\end{cases}$$

$$X=\begin{cases} R, & R\leqslant 6.71,\\ R-0.263\sin[1.075(R-6.71)], & 6.71\leqslant R\leqslant 8.17,\\ R-0.263\exp[-0.85(R-8.17)^2], & 8.17\leqslant R\leqslant 1.2R_1;\end{cases}$$

$$V(R)=-1.94\times10^{-3}+(R-1.2R_1)\{4.44\times10^{-4}-(R-1.5R_1)[8.84\times10^{-6}-(R-1.2R_1)1.06\times10^{-4}]\},$$

$$1.2R_1\leqslant R\leqslant 1.5R_1,$$

$$V(R)=-8875R^{-6},\quad 1.5R_1\leqslant R.$$

Usually the imaginary part of the potential is taken as a single exponential. However in order to obtain a good fit to the measured differential cross section, we had to use a $\Gamma(R)$ of the following form: $\Gamma(R)=1.9\times10^{-2}\exp[-0.9(R-5.93)^2]+3.27\times10^3\exp(-2.26R)$. The large number of free parameters in the double Morse function was absolutely essential to obtain the good fit seen in Fig. 1. The width $\Gamma(R)$ is given in Fig. 2 by the dot-dashed line. On the right-hand ordinate the transition frequency $[\Gamma(R)/\hbar]$ is indicated. The values ϵ_i and internuclear distances r_i of the three extrema are $\epsilon_1=-3.8\pm0.5$ meV, $r_1=10.41\pm0.35$ a.u., $\epsilon_2=25.5\pm2.5$ meV, $r_2=6.71\pm0.20$ a.u., and $\epsilon_3=16.8^{+0.4}_{-0.25}$ meV, $r_3=5.96\pm0.20$ a.u. The potential is determined and valid of course only at energies below 66 meV. Experiments with higher energies are in progress.

The rainbow peak is also apparent in the data of Refs. 3 and 4, but due to the limited resolution it appears only as a shoulder and not as a maximum in the differential cross section. It was therefore not recognized at that time, and a single Morse–spline–Van der Waals potential plus an assumed opacity function was used to fit the data. The question remains how uniquely a complex potential can be determined from an angular distribution. A correct quantum mechanical treatment has not been carried out before in atomic physics. The opacity analyses used in Refs. 3 and 4 cannot be applied in this case, because the strong absorption has a large effect on the differential cross section.[9] The proposed potential reproduces the small-angle oscillations, the rainbow peak, and the strong absorption at large angles over an energy range of a factor of three.

We were not able to devise a potential without the intermediate maximum which was compatible with our data. This maximum explains very easily two experimental results, which were difficult to explain with the older smooth potential.[1] First, the total ionization cross section varies only weakly with energy over the experimental range (30–600 meV). This is exactly, what one expects and calculates[9] from the proposed potential. All particles below a weakly energy-dependent impact parameter can overcome the barrier, reaching the region of large $\Gamma(R)$ where they are strongly absorbed. Second, the measured Penning electron energy distributions are narrow and nearly energy independent. The transition rate is proportional to $\Gamma(R)/v(R)$, where $v(R)$ is the local velocity. Most of the transitions do not occur near the repulsive wall as usually assumed, but around the potential maximum, because of the low velocity at this point. This gives rise to a narrow, nearly energy-independent electron energy distribution. An energy-independent double "edge effect" occurs classically, because the difference potential also shows the intermediate maximum.[8] No structure is expected in the electron spectra because of the large de Broglie wavelength, the large value of $\Gamma(R)$, and the limited experimental resolution. The position of the peak of the electron spectra is also compatible with the proposed potential. Calculations and a more detailed discussion of these effects will be given elsewhere.[9]

The velocity dependence of the total ionization cross section and of the Penning electron spectra of Ar, Kr, and Xe all show the same behavior.[1,15] The interaction potentials of $He(2^1S)$ with the heavier rare gases are therefore probably similar to that with argon. At very small distances the He*-Ar interaction is predominantly a $He^+ - Ar$ interaction and the potential must therefore be similar to that proposed by Olson[16] in this region.

We have also measured angular distributions for the $He(2^3S)+Ar$ and have obtained the corresponding optical interaction potential.[9] The potential, which does not have an intermediate maximum, gives a very good fit to the experimental total ionization cross section, and explains also the dependence of the Penning electron spectra on the collision energy. The experimentally observed differences between the two spin systems can now be rationalized completely by the difference in their interation potentials.[17]

Support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Till Ebding for fruitful discussions.

[1] R. D. Rundel and R. F. Stebbings, in *Case Studies in Atomic Collision*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1972), p. 549; A. Niehaus, Ber. Bunsenges. Phys. Chem. 77, 628 (1973); H. Hotop, Radiat. Res. 59, 379 (1974); C. Manus, to be published.

[2] C. Mahaux and H. A. Weidenmüller, *Shell-Model Approach to Nuclear Reactions* (North-Holland, Amsterdam, 1969).

[3] C. H. Chen, H. Haberland, and Y. T. Lee, J. Chem. Phys. 61, 3095 (1974).

[4] H. Haberland, C. H. Chen, and Y. T. Lee, in *Atomic Physics 3*, edited by S. J. Smith and D. K. Walters (Plenum, New York, 1973), Vol. 3, p. 339.

[5] J. Ross and E. F. Green, in *Molecular Beams and Reaction Kinetics*, edited by Ch. Schlier (Academic, New York, 1970), p. 86; D. Micha, in *Modern Theoretical Chemistry*, edited by W. H. Miller (Plenum, New York, to be published), Vol. 3.

[6] M. T. Leu and P. E. Siska, J. Chem. Phys. 60, 2179 (1974).

[7] H. Nakamura, J. Phys. Soc. Jpn. 26, 1473 (1969).

[8] W. H. Miller, J. Chem. Phys. 52, 3563 (1970).

[9] B. Brutschy, H. Haberland, and K. Schmidt, to be published.

[10] A. P. Hickman and H. Morgner, to be published.

[11] K. W. Ford and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 259 (1959); J. P. Toennies, in *Physical Chemistry, an Advanced Treatise*, edited by D. Hinderson (Academic, New York, 1973), Vol. IV, Chap. 6.

[12] P. R. Bevington, *Data Reduction and Error Analyses for the Physical Sciences* (Mc Graw-Hill, New York, 1969).

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

[14] K. L. Bell, A. Dalgarno, and A. E. Kingston, J. Phys. B. 1, 18 (1968).

[15] E. Illenberger and A. Niehaus, Z. Phys. Chem., Abt. B 20, 33 (1975).

[16] R. E. Olson, Phys. Rev. A 6, 1031 (1972).

[17] A preliminary version of the $He(2^3S)+Ar$ potential has been used in Ref. 10.