Dr. U. Buck, Dr. H. O. Hoppe, Dr. F. Huisken and Prof. H. Pauly (*Göttingen*) said: We would like to give an example for a direct inversion of differential cross section data to the potential ¹ mentioned in the Introduction by Prof. J. P. Toennies. We have measured the differential cross section for the system Li–Hg in the energy range of $30-50 \times 10^{-14}$ erg. There is a special reason to study this system. Early attempts with relatively restricted input data have given potential parameters which vary over wide ranges. Furthermore a potential derived by Olson from glory scattering data and rapid oscillations ² differs significantly ³ from the other alkali mercury potentials obtained by inversion.⁴

In order to resolve the rainbow structure, an experimental arrangement has been used which provides a velocity resolution of about 3 %. Both beams have been analysed by self calibrating velocity selectors so that the absolute value of the relative velocity is determined within 1 %.

Fig. 1 shows the experimental results. The quantity $I(\theta)$ which is proportional to the differential cross section, multiplied by $\sin \theta$, is plotted versus the deflection



FIG. 1.—Measured differential cross section for Li on Hg in centre of mass coordinates for $E = 48.9 \times 10^{-14}$ erg.

- ¹ U. Buck, J. Chem. Phys., 1971, 54, 1923.
- ² R. Olson, J. Chem. Phys., 1968, 49, 4499.
- ³ W. Stwalley, J. Chem. Phys., 1971, 55, 170.
- ⁴ U. Buck and H. Pauly, J. Chem. Phys., 1971, 54, 1929; U. Buck, M. Kick and H. Pauly, J. Chem. Phys., 1972, 56, 3391.

angle θ in the centre of mass system. Four rainbow extrema with well resolved rapid oscillations over the whole angular range are displayed. These data, taken at six different energies, have now been used to obtain the potential by direct inversion in a unique way. In the first step the deflection function is constructed using the following input data :

the positions of the rainbow extrema,

the positions of the rapid oscillation,

the maximum phase shifts from the glory scattering (which agree very well with our extrapolated values from the supernumerary rainbows),

the backward scattering near the first rainbow maximum,

the calculated van der Waals constant.¹

In the second step, the potential is determined by direct integration over the weighted deflection function.² The results are shown in fig. 2. The potential resulting from each of the different energies is the same to within the experimental error. The minimum distance r_m and the corresponding well depth are 3.00 Å and 16.9×10^{-14} erg, respectively.



FIG. 2.—Potentials for LiHg obtained by the inversion of differential cross section measured at different energies.

Our accurate results confirm the potential of Olson. This means that the potential of Li-Hg differs significantly from the other alkali-mercury potentials in contrast to the behaviour, for instance, of the rare gas potentials. Both size parameters and the form are different. Another interesting feature is that the contribution of the C_8r^{-8} term for Li-Hg is small compared with the other systems.

Dr. R. Gengenbach, Prof. J. P. Toennies, Dr. W. Welz and Dr. G. Wolf (*Göttingen*) said : As pointed out in the paper by Bickes *et al.* the value for the well depth ε for the

¹ W. C. Stwalley and K. L. Kramer, J. Chem. Phys., 1968, 48, 5555.

² U. Buck, J. Chem. Phys., 1971, 54, 1923.

system H-He reported there is not very precise because of the relatively large beam energies used in these experiments. In a computational study of the effect of various ε -values on the low velocity (<1000 m/s) integral cross section a Ramsauer-Townsend effect was found to occur for a certain range of ε -values.¹ To measure the low velocity integral cross section we have developed a liquid N₂ cooled r.f. discharge source to produce a " cold " H-atom beam. With this source we have been able to extend the velocity range down to 400 m/s ($E_{\rm em} = 0.75$ meV). A liquid He cooled (5 K) scattering chamber was used to reduce the target motion. Fig. 1 shows the measured cross section for H-He and H₂-He. The decrease in the H-He cross section at low velocities provides the first clear evidence for a Ramsauer-Townsend effect in atom-atom scattering.² It is not observed for H₂-He, where the measured points are well fitted by the calculated curve based on a potential reported earlier.³



FIG. 1.—Measured integral cross sections for H-He (\bullet) and H₂-He (+) at 5 K target temperature as a function of the primary beam velocity. Comparison is made to calculated effective cross sections based on the potential model given in ref. (3) for H₂-He and in ref. (1) for H-He with $\varepsilon = 0.46$ meV. The horizontal bars at the bottom indicate the full half width of the distribution of relative velocities.

The H-He measurements can be fitted by two MSV potentials with identical repulsive regions but different wells characterized by $\varepsilon = 0.46$ and 0.69 meV. The system D-He, for which a minimum only occurs for $\varepsilon = 0.46$, has also been studied. A minimum was observed so that all the measurements are consistent only with $\varepsilon = 0.46$.

Prof. V. Aquilanti, Prof. G. Liuti, Dr. F. Vecchio-Cattivi and **Prof. G. G. Volpi** (*Perugia*) said : Some time ago, we measured the absolute total cross sections for elastic scattering of H atoms with Ar, Kr and Xe,⁴ in a velocity range also covered

- ¹ R. Gengenbach, Ch. Hahn and J. P. Toennies, Phys. Rev. A, 1973, 7, 98.
- ² A Ramsauer-Townsend effect has also recently been observed for He⁴-He⁴ by R. Feltgen, H. Pauly, F. Torello and H. Vehmeyer, *Phys. Rev. Letters*, to be published.
- ³ R. Gengenbach and Ch. Hahn, Chem. Phys. Letters, 1972, 15, 604.
- ⁴ V. Aquilanti, G. Liuti, F. Vecchio-Cattivi and G. G. Volpi, Chem. Phys. Letters, 1972, 15, 305.

Published on 01 January 1973. Downloaded by Simon Fraser University on 21/06/2017 05:23:40.

by the more extensive measurements of the Göttingen group.¹ In this range, given a potential model, the velocity dependence of cross sections yields the product εr_m , while their absolute values allow the estimate of r_m : our analysis in terms of potentials of the Lennard-Jones family leads to apparently good fits of the data, although it fails to reproduce the known long range behaviour. Therefore it is not surprising that Toennies' analysis in terms of a potential which is similar to a Lennard-Jones (12, 6), via the *ad hoc* assumption of proper long range behaviour by a set of combining



FIG. 1.—Dependence of cross section Q on velocity for O₂-Ar and O-Ar collisions, as $Qv^{2/5}$ against log v. The solid lines have been calculated for a Lennard-Jones (12, 6) potential with the parameters shown and for a scattering chamber temperature of 77 K.

rules, yields a good fit to the velocity dependence of cross sections but predicts absolute values in disagreement with our measured ones. Notwithstanding these gross drawbacks of simple model potentials in describing these systems, we must realize that the experiments with such unstable species as hydrogen atoms appear to be still in a stage which prevents the use of more sophisticated analysis. Introduction of more flexible potential forms, with additional parameters, must presumably wait for improvements in the molecular beam techniques. The present situation resembles closely that of experiments with alkali atoms a dozen years ago: of course, differential measurements and/or detection of quantum effects would help considerably.

¹ R. W. Bickes, Jr., B. Lantzsch, J. P. Toennies and K. Walaschewski, this Discussion.

In this connection, we present in fig. 1 some results on the scattering of oxygen atoms and molecules by argon. The apparatus is the same as described earlier¹; mass spectrometric detection allowed the simultaneous measurement of cross section for O and O₂, and the relative scale of the data plotted in the figure for the two systems is therefore accurate. Although the potential parameters given in the figure, as well as the calibration of the ordinate scale, rely on a preliminary analysis of the data, the glory undulations superimposed on a $v^{-2/5}$ dependence on velocity are clearly seen.

Dr. K. P. Lawley (Edinburgh University) said: We have just had three examples of elastic scattering involving atoms that are not in an S state; $O({}^{3}P_{2,1,0})$ (Volpi), $I({}^{2}P_{\frac{1}{2}})$ (Lee) and Hg*(${}^{3}P_{2}$) (Davidson *et al.*). In such cases several potentials evolve from the separated atoms if J and m_J are not selected. In molecular spectroscopic terms these states can be labelled by their Λ and Ω values. If, as in the case of heavier atoms, the J state is known, the number of molecular states that are adiabatically accessible is much reduced and they probably have a common Λ value. If the atomic partner is in a ${}^{1}S$ state there will be 2J-1 such potential curves correlating with a given J state. It is therefore interesting that in all three examples quoted above structure was observed in either the total or differential cross section. The simplest deduction is that the potentials of states that differ only in Ω —and apparently, in the case of O, in Λ —are rather similar. In the case of scattering from excited states (Hg*) there is however, the possibility that selective quenching might be responsible for some simplification of the scattering pattern. One must in any case remember that in these thermal energy experiments the repulsive (i.e., negative) branch of the potential is not really being sampled and it is just this region that a larger splitting of the manifold of potentials might be expected.

Dr. J. F. Ogilvie and **Mr. R. W. Davis** (*Memorial University of Newfoundland*) said: We have been able to deduce some generalisations about the nature of the potential energy function, in the region of the energy minimum, between very weakly bound atoms. We have transformed other published potentials, derived from molecular beam and spectroscopic experiments and from thermal and transport properties, into the Dunham² form:

$$(U/D_{\rm e}) = a'_0 x^2 [1 + \sum_{i=1}^{n} a_i x^i].$$

Here U = potential energy, $D_e =$ depth of potential well, $x = (R - R_e)/R_e$, R = instantaneous internuclear separation, and $R_e =$ separation at the energy minimum; a'_0 and a_i ($i \ge 1$) are parameters adjusted to fit the data for the potential function, from whatever source. This Dunham function can be used to express a real potential, smoothly varying in the region of interest, to the required accuracy in a given range of X by employing sufficient terms in the summation.

Calder and Ruedenberg ³ discovered useful generalisations for strongly bound diatomic molecules in their ground states. For hydrides XH and non-hydrides XY, a_1 and a_2 in the Dunham function were found to be relatively constant within these classes of molecules. We add two further classes M_2 and A_2 which consist of alkaline-

¹ V. Aquilanti, G. Liuti, E. Luzzatti, F. Vecchio-Cattivi and G. G. Volpi, Z. phys. Chem., 1972, 79, 200.

² J. L. Dunham, Phys. Rev., 1932, 41, 721.

³ G. V. Calder and K. Ruedenberg, J. Chem. Phys., 1968, 49, 5399.

earth dimers Mg₂ and Ca₂, and noble-gas dimers He₂, Ne₂, Ar₂ and Kr₂, respectively. For these molecules, $92 < D_e < 11\ 000\ J\ mol^{-1}$. The values are listed in the table :

	ХН	XY	M ₂	A_2
$-a_1$	2.4 ± 0.1	3.2 ± 0.1	4.9 ± 0.2	7±0.5
a_2	3.8 ± 0.2	6.4 ± 0.75	18	26 ± 4

The A_2 molecules are formed from closed-shell atoms; therefore the values obtained for them may be appropriate and transferable to the non-directional part of the interaction between ordinary non-polar molecules. We believe these new values may find application in the study of intermolecular forces, in particular possibly in the construction of empirical potential surfaces for elastic and inelastic collisions. Further details of the results will be published separately.

-