Orbiting Resonances in the Scattering of H Atoms by Mercury at Thermal Energies*

A. Schutte,† D. Bassi, and F. Tommasini
Istituto di Scienze Fisiche dell'Università, 16132 Genova, Italy

and

G. Scoles
Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada
(Received 31 July 1972)

The energy dependence of the integral elastic-collision cross section for scattering of hydrogen and deuterium atoms by mercury at thermal energies has been measured. For hydrogen at ca. 1.4×10^5 cm sec^{-1} evidence has been found for a structure superimposed on the glory pattern. This can be attributed to two overlapping orbiting resonances and represents the first observation of quasibound vibrational-rotational levels of a diatomic molecule through scattering measurements.

In 1966 Bernstein[1] pointed out the complementary nature of the information about long-range interatomic potentials yielded by two different experimental techniques for observing quasibound vibrational-rotational levels of diatomic molecules.[2-4] The methods are (a) the spectroscopy of these rotationally predissociating levels, and (b) the observation of structure caused by these levels (here called orbiting resonances) in the velocity dependence of the cross section for the scattering of the constituent atoms. The first of these techniques has long been used as a means of determining molecular dissociation energies,[5] but until the present, no unambiguous scattering measurements of this phenomenon have been reported.

In 1967 Stwalley, Niehaus, and Herschbach[6] reported tentative evidence for orbiting resonances in Hg-H scattering. However, their data did not show clearly resolved resonances and the authors emphasized the uncertainty of their interpretation. Feltgen[7] later made an extensive study of the effects of the different kinds of averaging which would enter into the experimental observation of these resonances, but his attempt to detect them in the He-Kr system was unsuccessful. More recently Collins and Hurlbut[8] claimed to have observed an orbiting resonance in the scattering of He and N_2. However, they were not able to resolve either the position or the width of the apparent structure, and hence their conclusion must be regarded as somewhat speculative. In contrast, the present results show clear evidence of an orbiting resonance in the system Hg-H at a relative velocity of ca. 1400 m sec^{-1}. Over the same velocity range, the limited apparatus resolution prevented the observation of such resonances in the analogous Hg-D system.

The experimental apparatus, shown schematically in Fig. 1(a), consists of two vacuum chambers separated by a collimator (C_0). In the first chamber a classical atomic hydrogen beam is produced by a rf discharge source (S_1). The temperature of this beam is normally 500°K, but it can be lowered to 300°K by cooling the tip of the source [see Fig. 1(a)]. In the second chamber a shutter (*SH*) and a chopper (*CH*) are situated in front of a cryopumped multichannel Hg secondary beam source (S_2) which can be rotated under vacuum into and out of the path of the primary beam. The secondary beam is inclined at about 73° relative to the primary beam in order to improve the velocity resolution.[7] The beam collimator scheme is presented in Fig. 1(b); the dimensions and temperatures of the collimators are given in Table I. The velocity selector (*VS*) has the characteristics $V_{\max} = 5000$ or 2500 m sec^{-1} at 500 Hz in the two possible senses of rotation, the corresponding full width at half-maximum $\Delta V/V$ being 8.5% and 3.2%, respectively. The double band pass ensures a careful calibration of the velocity scale.

Studies in this laboratory have demonstrated[9] that a low-temperature bolometer[10] is the best available detector of atomic hydrogen beams. Its ability to detect a particle flux as amall as 2×10^7 atoms cm^{-2} sec^{-1} was essential to the success of the present experiment. A commercially available ribbon-shaped bolometer detector (*B*) operating at liquid-helium temperatures was used here. As was shown in Ref. 9, the energy given to the bolometer surface by the H atom beam depends on the chemical composition of the surface. While a surface of oxygen molecules gives a very high signal, it tends to be time dependent

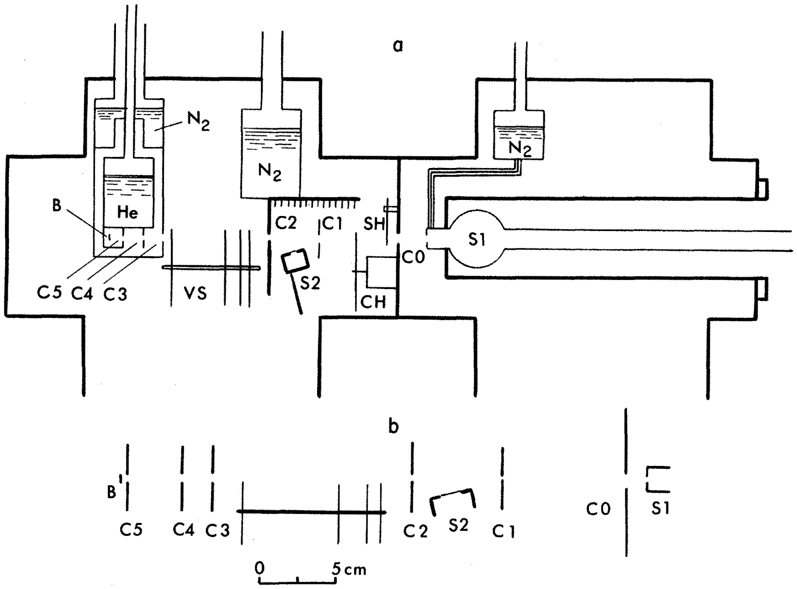

FIG. 1. (a) Experimental apparatus. The symbols are explained in the text. (b) Experimental collimation scheme. Collimator dimensions and temperatures are listed in Table I.

since the O_2 molecules are readily sputtered off the surface. To remove this instability, a small oxygen leak was introduced into the detection chamber to supply fresh O_2 continuously to the bolometer surface. This increased the pressure in the chamber from 4 to 10×10 Torr.

Signal integration was performed with standard lock-in techniques. The time constant was normally 1 sec. The detector noise equivalent power of 10^{-13} W $\mathrm{Hz}^{-1/2}$ corresponds to a minimum detectable beam of 2×10^7 atoms sec^{-1} cm^{-1}. The H_2 used was $\geqslant 99.99\%$ pure.

The results are shown in Figs. 2 and 3; three and four glory extrema[11] were resolved for HgH and HgD, respectively, which correlate with previous results.[6] The marked deviation from the normal undulatory pattern seen on the HgH glory maximum centered near 1500 m sec^{-1} is attributed to one or more orbiting resonances. This conclusion is confirmed by comparisons with theoretical cross-section curves for Hg-H and Hg-D calculated using an interaction potential which Stwalley[12] obtained on combining theoretical C_6 and C_8 dispersion coefficients with an isotopically combined Rydberg-Klein-Rees curve for the bowl of the potential well. The good agreement between these calculated curves and experiment (see Figs. 2 and 3) is in marked contrast with the very poor agreement obtained using the potential proposed by Hulburt and Hirschfelder,[13] some modifications of it made by Stwalley,[14,6] and other modifications tried by us.

TABLE I. Dimensions and temperatures of the primary beam collimators.

Collimator	Dimensions (mm)	Temperature (°K)
S_1	5 (diam)	500–300
C_0	1.2 (diam)	300
C_1	0.5×3	300
C_2	3 ×5	77
C_3	3 ×5	77
C_4	2 ×5	1.7
C_5	1 ×5	1.7
B	0.5×5	~2.5

Figure 2(b) shows the contributions to the integral cross section from the partial waves which are important in the region of interest. They imply that the observed structure at ca. 1400 m sec^{-1} is due to either the ($V=4$, $l=9$) or the ($V=3$, $l=10$) quasibound level of HgH, or a combination of the two. However, the experimental and theoretical curves in Figs. 2 and 3 are not really directly comparable, since the calculation of the latter did not include averaging to take account of the finite experimental resolution.[7] Moreover a rather small deviation from reality in Stwalley's potential[12] can shift the resonances an appreciable amount. This precludes a final determination of the relative contributions of the different

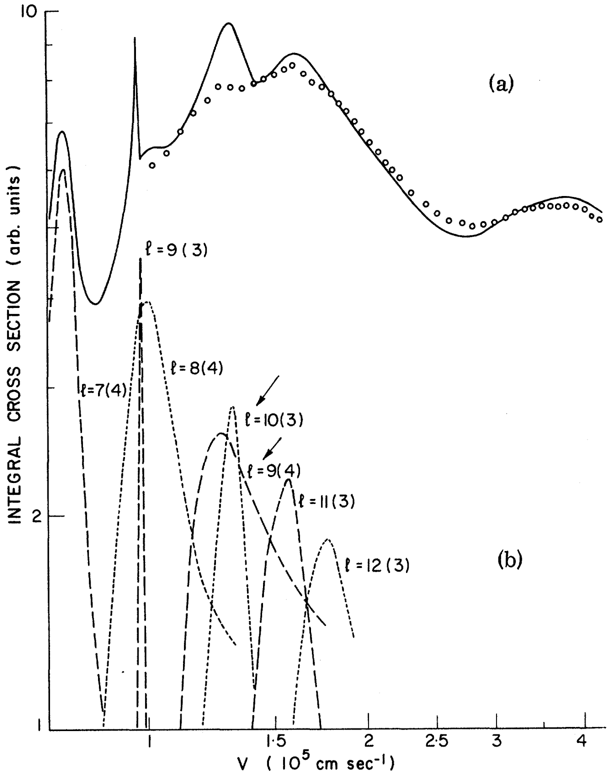

FIG. 2. (a) Integral elastic collision cross section for Hg + H as a function of the relative velocity. Circles, experimental points; solid curve, calculated values (see text). The statistical error is about the same for all points and corresponds to the height of the experimental points. (b) Contributions to the integral cross section from the important partial waves in the relative velocity range 1000–2000 m sec^{-1}. The numbers within the parentheses indicate the vibrational level.

partial waves to the observed resonance structure. However, there can be little real doubt about the identification of this structure with orbiting resonances.

A more extensive theoretical analysis of the present results is now in progress. It will take account of the finite apparatus resolution and attempt to obtain better agreement between theory and experiment by making small alterations in the long-range part of Stwalley's potential. This should yield both absolute assignments for the source of the observed resonance structure and an improved potential for the interaction of Hg with H or D.

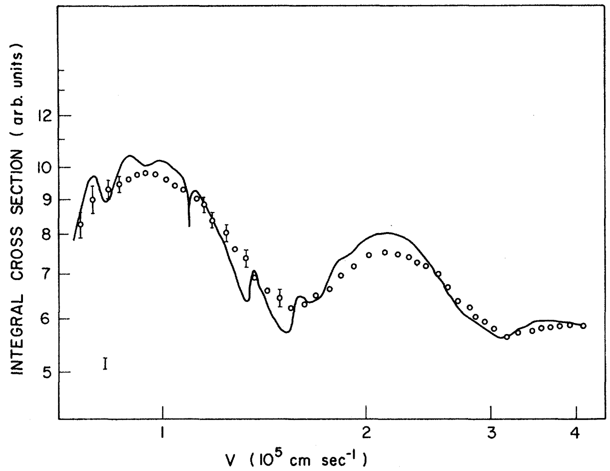

FIG. 3. Integral elastic collision cross section for Hg + D as a function of the relative velocity. Circles, experimental points; solid curve, calculated values (see text). Unless indicated the statistical error is smaller than the bar reported in the lower left corner of the figure.

It is a pleasure to thank Dr. W. C. Stwalley for very useful correspondence and for giving us his new potential prior to publication. We are indebted to Dr. M. G. Dondi, Dr. R. J. LeRoy, Dr. A. C. Levi, and Dr. G. Viano for many helpful discussions and to L. Mattera for assistance in making the measurements. We are also grateful to M. Castoldi, A. Parodi, A. Pozzo, O. Rosati, and C. Tassistro for their invaluable and prompt technical assistance. Dr. R. J. LeRoy kindly revised the manuscript.

---

[*] Work supported by the NATO Office for Scientific Research under Grant No. 419 and carried out with the facilities of the Gruppo Nazionale di Struttura della Materia, a division of the Italian National Research Council.

[†] Deceased on 29 March 1972. He was on leave of absence from the Kamerlingh Onnes Laboratorium, Leiden, The Netherlands. This work was intended to be part of his thesis.

[1] R. B. Bernstein, Phys. Rev. Lett. 16, 385 (1966).

[2] G. Büttenbender and G. Herzberg, Ann. Phys. (Leipzig) 21, 577 (1934/35).

[3] R. Schmid and L. Gerö, Z. Phys. 104, 724 (1937).

[4] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, (Chapman and Hall, London, 1968), 3rd ed.

[5] R. J. LeRoy and R. B. Bernstein, J. Chem. Phys. 54, 5114 (1971).

[6] W. C. Stwalley, A. Niehaus, and D. R. Herschbach, in *Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, 1967, Abstracts of Papers*, edited by I. P. Flaks and E. S. Solovyov (Nauka, Leningrad, 1967), p. 639.

[7] R. Feltgen, thesis, Bonn University, Bonn, 1970 (unpublished), pp. 58–75.

[8] F. G. Collins and F. C. Hurlbut, J. Chem. Phys. 56, 2609 (1972).

[9] G. Marenco, A. Schutte, G. Scoles, and F. Tomma-

sini, J. Vac. Sci. Technol. 9, 824 (1972).

[10] M. Cavallini, G. Gallinaro, and G. Scoles, Z. Naturforsch. 22a, 413 (1967).

[11] R. B. Bernstein and T. J. O'Brien, Discuss. Faraday Soc. 40, 35 (1965).

[12] W. C. Stwalley, private communication.

[13] H. M. Hulburt, J. O. Hirschfelder, J. Chem. Phys. 9, 61 (1941).

[14] W. C. Stwalley, thesis, Harvard University, 1968 (unpublished).

Practicable X-Ray Amplifier

R. A. McCorkle
East Carolina University, Greenville, North Carolina 27834

(Received 25 July 1972)

Inverted populations of practical interest in the x-ray region are obtainable from selective inner-shell vacancy production in intermediate-energy ion-atom collisions. A high-current ion beam swept at nearly the speed of light along the length of an extended foil provides an active region in synchronization with a resonant x-ray pulse traveling parallel to the foil surface. Significant amplification may be realized with presently available ion sources.

Means of creating population inversions at vacuum uv and x-ray wavelengths are now available and system designs for achieving amplified x-ray emissions are realizable.[1] The large cross sections[2] for selective production of atomic inner-shell vacancies by heavy-ion bombardment at intermediate energies (~1 keV/amu) of metal targets indicate an obvious mechanism. The physical process is thought to be an electron promotion mechanism that occurs at level crossings in the quasimolecule formed during the collision, and/or rotational excitation.[3] The vacancies produced may occur in the ion or the atom or both. Thus for ions passing through a thin foil, on the downstream side of the foil a significant number of ions will contain inner-shell vacancies. By a judicious choice of collision partners as well as beam energy and foil thickness, population inversions of interest may be achieved. Moreover, by sweeping the ion beam along the length of an extended target, such population inversions may be obtained in synchronism with a traveling wave front due to radiative decay of the states produced. Such a system would be capable of amplifying by stimulated emission this wave front advancing in the direction of sweep of the beam. Systems of this nature would be of interest when operated in a single-pass mode with no cavity,[4] or when placed in a suitable x-ray laser cavity (such as is now being investigated[5] or may be available at the time of realization of this system).

For ion-atom combinations such that inner-shell energy levels of interest match, ion to atom, cross sections for the selective production of vacancies in these shells are given approximately by taking for the level-crossing radius a value equal to the sum of the radii of the two electronic shells involved.[2,6] As an example, the match in energy between the carbon K shell and the argon L shell allows selective vacancies to be produced in the L shell of argon. In particular, measurements[7] show that for bombarding energies below ~80 keV effects of double L-shell excitation are not observed. Furthermore, it was found that at an ion energy of ~50 keV, the resulting x-ray spectra indicated the strong predominance of the 224-eV line due to a $3s \rightarrow 2p$ transition. The radiative lifetime of this transition may be taken as $\sim 2.8\times10^{-11}$ sec[8] and a fluorescence yield of 1.67×10^{-3} is reasonable.[9]

A system design is indicated in Fig. 1. A high-current, well-focused, heavy-ion beam, in the energy range of interest (30 to 500 keV), is deflected by a parallel-plate transmission system

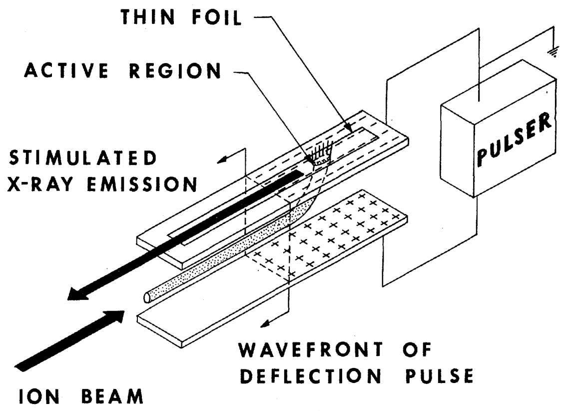

FIG. 1. Schematic of x-ray traveling wave amplifier.