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Elastic Scattering of Atoms and Molecules in the Thermal Energy Range

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Abstract

The goal of research on elastic scattering of atomic (or molecular) beams is the elucidation of the interaction potential V(r). The present discussion is confined to thermal energy collisions (< 1 ev), sensitive primarily to the attractive part of the potential. Studies of the velocity dependence of the differential and total elastic scattering cross sections have yielded information as follows: (1) The functional form of the long-range attraction : $V \sim -C/r^6$, from differential cross sections $I(\theta)$, at low angles: $I(\theta) \propto \theta^{-7/3}$. (2) The attractive potential constant C, from total cross sections: $Q \propto (C/v)^{2/5}$. (3) The depth of the potential well ϵ, from the rainbow effect in $I(\theta)$: $\theta_r = f(\frac{1}{4}\mu v^2/\epsilon)$. (4) The equilibrium separation r_m, from de Broglie interference producing undulations in $I(\theta)$. (5) The product ϵr_m, from extrema in $Q(v)$, and thus r_m (from absolute Q's). (6) Observation of m maxima in plots of $vQ^{5/2}$ vs. v^{-1} (termed elastic impact spectra) implies the existence of at least m bound states (discrete vibrational levels of zero angular momentum for the composite system).

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Introduction

A. Scope

The research program in which we have been engaged has involved experimental and theoretical studies of atomic and molecular beam scattering in the thermal energy regime (i.e., collision energies in the range 10^{-3} - 1 ev). Our interest is the elucidation of interatomic (and intermolecular) forces via elastic scattering measurements.

It has long been recognized that thermal-energy scattering measurements are sensitive primarily to the long range attractive part of the interaction potential[1]; however, it has recently been shown that they also evidence, but in a more subtle way, the influence of the short-range repulsion[2].

In the present paper our own low-energy scattering studies and closely related work by others are reviewed. We shall be concerned mainly with the velocity dependence of the differential and total elastic cross sections for scattering of atoms by atoms and by simple molecules. The analysis of such experiments in terms of the interaction potential will be discussed. The discrepancy between the theoretically calculated long-range inverse-sixth-power potential constants and those deduced from the experiments will be considered. Finally, the manifestation in the elastic atom-atom impact spectra of the bound states for the composite system will be discussed.

B. Interaction Potentials

Up to the present time most of the experimental observations have been analyzed in terms of simple central potentials[3] of the form

$$V(r) = V_{rep}(r) + V_{attr}(r) \qquad (1)$$

where $$V_{attr}(r) = -C^{(s)} r^{-s} \quad \text{(with } s = 6\text{, usually)} \qquad (2)$$

and $V_{rep}(r) = C^{(exp)} e^{-\alpha r}$ or $C^{(n)} r^{-n}$ (with α or $n > 6$, usually) (3)

(all C's are positive quantities).

In a few cases the Morse potential has been used. Sometimes an additional r^{-8} term has been added to Eq. 2 and occasionally a "tailored" many-parameter function has been investigated.

We write the more frequently used potentials in reduced notation, as follows:

Lennard-Jones (n,6): $V^*(z) = \left(\frac{6}{n-6}\right) z^{-n} - \left(\frac{n}{n-6}\right) z^{-6}$ (4)

Exponential (α,6): $V^*(z) = \left(\frac{6}{\alpha-6}\right) e^{-\alpha(z-1)} - \left(\frac{\alpha}{\alpha-6}\right) z^{-6}$ (5)

Morse (a): $V^*(z) = e^{a(1-z)} - 2e^{\frac{a}{2}(1-z)}$ (6)

where $z = r/r_m$, $V^* = V/\epsilon$; r_m is the position of the minimum in the potential and ϵ is the depth of the well. The parameters n, α and a are measures of the steepness of the repulsion.

For intercomparisons in the region of the well, common curvature at the minimum requires $6n = 6\alpha(\alpha-7)/(\alpha-6) = a^2/2$. For matching asymptotically at large r we require $n = \alpha$; the Morse function, of course, cannot properly represent the long-range interaction.

Many analyses of scattering results have been based on the L.-J.(12,6) potential, usually written in a simple alternative form:

$$V^*(x) = 4(x^{-12} - x^{-6}) \quad (7)$$

where $x \equiv r/\sigma$ and σ is the position of the first zero of the potential, related to r_m by: $r_m/\sigma = 2^{1/6}$.

For interactions between molecules, angle dependent potentials are required [3a,5]; these are often written in the form of Legendre expansions. For the atom-diatomic molecule case, for example, one may write

$$V(r,\theta) = V_{rep}(r) \sum_n b_n P_n(\cos\theta) + V_{attr}(r) \sum_n a_n P_n(\cos\theta) \quad (8)$$

where θ is the angle between the internuclear axis of the molecule and the line connecting the center-of-mass of the molecule with the atom; a_n and b_n are "asymmetry coefficients" whose sign and magnitude are to be determined. Averaging over all orientations (taking advantage of the orthogonality of the Legendre functions), Eq. 8 reduces to Eq. 1. Usually only the leading terms in Eq. 8 are retained:

$$V_{rep.}(r,\theta) = V_{rep.}(r)\left[1 + b_1 P_1(\cos\theta) + b_2 P_2(\cos\theta)\right] \qquad (9)$$

(with the further simplification that for a homonuclear molecule $b_1 = 0$)

and $$V_{attr.}(r,\theta) = V_{attr.}(r)\left[1 + a_2 P_2(\cos\theta)\right]. \qquad (10)$$

The omitted term in P_1 is zero for a homonuclear molecule and should be negligible[6] also for a heteronuclear diatom in the region of large r where the r^{-6} dependence (Eq. 2) is valid.

The long-range asymmetry parameter may be estimated from the anisotropy of the polarizability[3a,3b]

$$a_2 \approx (\alpha_{\parallel} - \alpha_{\perp})/(\alpha_{\parallel} + 2\alpha_{\perp}) \qquad (11)$$

Some experimental scattering results[7] bearing on the asymmetry in the attractive part of the potential are now available.

1. Low Angle Differential Cross Sections: Evidence for Inverse Sixth Power Attraction.

On the basis of classical small-angle deflection theory[8], for a potential of the form of Eq. 2, the low-angle differential solid-angle scattering cross section should be given by

$$\frac{d\sigma(\theta)}{d\Omega} = I(\theta) = g(s)\left[\frac{C^{(s)}}{E}\right]^{2/s}\frac{\csc\theta}{\theta^{1+2/s}} \propto \theta^{-2(1+1/s)} \qquad (12)$$

where $E = \frac{1}{2}\mu v^2$ and g(s) is a numerical constant; the substitution

$\sin\theta \cong \theta$ has been made in the last step. For the case of $s = 6$, the low angle dependence[2d] becomes

$$I(\theta) \propto \theta^{-7/3} \qquad (13)$$

The unphysical singularity at $\theta = 0$, leading to an infinite total cross section (Q_{total}) is a well-known failure of the classical treatment. However, Massey and Mohr[1a] showed that a quantum mechanical approach yielded a finite value of $I(0)$ and Q. Pauly[9a] extended this work and deduced the low-angle limiting form of the quantum differential cross section. The quantum treatment is required for angles smaller than a certain value, say $\theta^* \cong 2/kr_0$, where $r_0 \equiv (Q/\pi)^{1/2}$ and $k \equiv \mu v/\hbar$ as usual. For molecular collisions at thermal energies, θ^* is of the order of minutes of arc; above this angle the classical low angle cross section equations should be applicable.

Helbing and Pauly[9] investigated with high resolution the very low angle ($< 1^o$) elastic scattering behavior for a number of systems, using Maxwellian beams and scattering gases; they verified the expected transition from a quantum to a classical angular dependence at angles of the proper magnitude. As a byproduct of their work it is possible to set a limit on the amount δQ, by which "apparent" values of the total cross section (for a given angle of minimum resolution θ_m) are smaller than the true values, Q, corresponding to $\theta_m = 0$. It was shown[9a] that

$$\frac{\delta Q}{Q} \cong 0.02\,(\theta_m/\theta^*)^2 \qquad (14)$$

so that for θ_m of the order of θ^* the "resolution error" is not a serious one. This is important in connection with the evaluation of absolute values of total cross sections.

The behavior of the differential cross section in the "classical low angle region" (typically, $1 \leq \theta \leq 10^o$ c. of m.) has been studied using monoenergetic beams (i.e., with velocity selection). Fig. 1 shows

a few angular distribution curves [2d] (log-log plots of $I(\theta)$) for the scattering of K by Hg. The low angle slopes are close to the expected value of -7/3, confirming the inverse sixth-power long-range potential. Similar observations have been made for Cs-Hg [2d] and Li-Hg [10]. Plots of $\theta^{7/3} \cdot I(\theta)$ vs. θ are essentially horizontal (see Sec. 4) out to about 10^{o} (c. of m), except for experiments at higher relative velocities where the repulsive part of the potential begins to become important at relatively lower angles.

The accuracy with which such measurements establish the exponent $s = 6$ is only fair. Eq. 12 shows that an uncertainty of, say, ±1% in the measured slope of plots such as Fig. 1 (an optimistic estimate of the experimental error) leads to an uncertainty of about ±0.4 in s (near $s = 6$). Nevertheless, the experimental results to date offer no basis to doubt the inverse sixth-power dependence of the long-range part of the potential.

For systems of low reduced mass (experiments at sufficiently small k), interference effects [4b, 2f] in the angular distribution have been observed [10] (see Sec. 4), but the conclusions above remain unaltered.

2. Total Cross Sections and Relation to Potential Constants.

Massey and Mohr [1a] (MM) were the first to develop a usable approximation formula for the total elastic cross section for scattering by a potential of the form of Eq. 2. They employed the random phase approximation for the lower order phases and the Jeffreys-Born (JB) approximation for the higher order ones ($\eta < 1/2$). In the semiclassical limit when many phases (e.g., >100) are required in the partial wave calculation, the

"statistics" are quite good and the cross section is fairly well approximated. Schiff [11a] (S) and Landau and Lifshitz [11b] (LL) developed somewhat different approximation formulas. We have intercompared [2i] these treatments; all follow from the same assumption (i.e., the classical small-angle deflection function, thence the Jeffreys-Born phases via the semiclassical equivalence relationship [6]. All the formulas are of the same form, i.e.

$$Q^{(s)} = p(s)\left[C^{(s)}/kv\right]^{2/(s-1)} \qquad (15)$$

The coefficient p(s) is the same for the S and LL approximations. For s = 6, $p_{MM} = 7.547$ while $p_{SLL} = 8.083$. It now appears that the SLL approximation is somewhat superior to that of MM. Eq. 15 then yields

$$C^{(6)}_{SLL}(\text{erg cm}^6) = 5.676 \times 10^{-30} \cdot vQ^{5/2} \qquad (16)$$

with v in cm sec^{-1} and Q in cm^2. The analogous formula for $C^{(6)}_{MM}$ has, however, been the one more frequently used. The results may, of course, be readily corrected by applying a factor of 0.8425 to the reported values of $C^{(6)}_{MM}$.

The velocity dependence of the cross section predicted by Eq. 15 has been tested experimentally for a number of heavy particle systems. Plots of log Q vs. log v are linear, the slope is $-2/(s-1)$, yielding s. Pauly [13a] used a velocity-selected beam of K scattered by N_2; his plot had a slope of -2/5, from which s = 6, with an uncertainty of about ±0.2. (From Eq. 15 it is seen that this corresponds to an uncertainty of about ±4% in the slope.) Similar results were reported for K-N_2 by Schoonmaker [13b] and for K-Xe by Rothe et al.[13c] (For the case of KCl-N_2, however, an apparent value of s = 5.3 was reported [13b]; the discrepancy may possibly be due to an effect (transition to high velocity behavior) to be mentioned below.) From experiments on the temperature dependence of Q for the scattering of thermal beams of CsCl by Ar and various non-polar molecules,

the value of s = 6 was also confirmed [13d]. Recently Beck [2e] has measured the energy dependence of the low-resolution "classical cross section" for K-Kr; a log-log plot of this "cross section" vs. E had a slope of -1/3, corresponding to s = 6 (according to the classical treatment; cf. Eq. 11).

For systems of low reduced mass significant undulatory deviations from a monotonic $v^{-2/5}$ dependence of Q at low velocities have been observed [10,13c,14], as predicted [2f,g,i]. This is discussed below.

At higher velocities the direct influence of the repulsive part of the potential (Eq. 3) becomes important [2h,f,g], the velocity dependence of the total cross section changes from $v^{-2/5}$ to a nearly flat (e.g., $v^{-2/11}$) dependence at very high velocity. A JB-type treatment[*] of this transition to high velocity behavior has been carried out [2g,h].

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[*] The accuracy of these results is the same as that of the MM approximation. The analysis of Ref. 2i showed, however, that the latter suffers from a bias ranging from 7.1% in the "low velocity" region (s = 6) to 4.6% in the "high velocity" region (s = 12). This suggests that the accuracy of the values of Q_{JB} of Ref. 2h could be improved by correction upwards by a factor of 1.046.

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Fig. 2 shows a calculated curve [2g] (essentially log Q vs. log v) for a L.-J.(12,6) potential with a given set of parameters. Three features should be noted: (a) the low velocity undulatory deviations from the line of -2/5 slope (s = 6), (b) the transition region, where the "apparent s" is smaller (here 3.3), and Q is systematically lower than the extrapolation of the -2/5 line, and (c) the high velocity region, in which the slope approaches -2/11 (s = 12) and Q becomes greater than the

-2/5 extrapolation.[20] Experiments[14a] supporting this predicted behavior are analyzed in Ref. 4d.

The following procedure for the analysis of total cross section data is therefore recommended.[21] A log-log plot of $Q(v)$ is made, inspection showing the range of v over which the mean curve (through the undulations) has a slope of -2/5. Over this range (the so-called "low-velocity" region for which[22] $v \lesssim \epsilon\sigma/\hbar$) a plot should be made of the apparent value of $C^{(6)}$, say $C^{(6)}_{app}$ (calculated from the SLL formula (Eq. 16)) as a function of v^{-1} (in such a plot the extrema are nearly evenly spaced). $C^{(6)}$ is then taken to be the average value of $C^{(6)}_{app}$. In low energy experiments with Maxwellian beams the velocity-averaging has already been effectively accomplished, so that the influence of the repulsion has been largely removed. Thus $C^{(6)}_{app}$ should be close to the true value of $C^{(6)}$.[23]

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[23] It should be noted that until the paper by Berkling et al.[15] in which proper averaging procedures were developed, most authors reported results in terms of Q (or r_o) at specified beam and gas temperatures or at some "mean" relative velocity, $\bar{v}_r$ (defined differently by various workers). The new procedures[15] yield a definite $Q(v)$ from which one may evaluate $C^{(6)}_{SLL}$ via Eq. 16. (However, it should be noted than an experimental uncertainty of only 5% in r_o (10.2% in Q) introduces an uncertainty of some 28% in C.)

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We are now in a position to examine the experimental results, i.e., C values deduced from Q measurements. Pauly[4d] has reviewed cross sections up to 1961. It is not intended here to present an exhaustive survey, but rather to examine recent (since 1957) results on certain well-studied

systems, namely, those involving Li, K, Cs and the rare gases. Table 1 summarizes the results. Experimental values of C are either $C_{SLL}^{(6)}$ (as calculated from Q) or the product $4\epsilon\sigma^6$ (where L.-J.(12,6) parameters had been determined). Some data on scattering by N_2 are included for comparison. The experiments were carried out in laboratories at the Universities of Bonn (Refs. d,j) Brown (Ref. h), Columbia (Ref. k), Michigan (Ref. c) and at General Dynamics/Astronautics (Refs. b,f,i). Most of the data have been obtained with Maxwellian beams and scattering gases, but certain experiments have employed techniques of velocity selection and/or crossed beams. In one case[b] the results are independent of a knowledge of the density of the scattering gas (see Sec. 3).

As seen from Table 1, experimental C values are consistently larger than the theoretical predictions. Table 2 shows, however, that relative values of C are in reasonable accord. The discrepancy in the absolute values might possibly be due to a common systematic experimental error; clearly a serious effort to obtain a reliable absolute value of a "reference" cross section is needed. However, if one accepts the present experimental results it appears that the inverse sixth power attraction is stronger than that deduced from perturbation theory calculations. This question is being further considered by P. R. Fontana and the author (see paper following).

3. Rainbow Scattering and Depth of the Potential Well.

For any realistic interatomic potential (Eq. 1) with an attractive well, the classical deflection function $\Theta(b,E)$ exhibits a minimum, designated[2b] $\Theta_r(E)$, the "rainbow angle". (Here b is the impact parameter

Table 1. Alkali - Rare Gas Interaction Constants

Entries are values of 10^{58} x C (erg cm^6)

	Li		K		Cs		Ar	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
He	0.21 [a]	0.46 [b]	0.32 [a]	0.53 [c] 0.40 [d]	0.36 [a]	0.85 [c] 0.40 [d]	0.095 [e] 0.11 [g]	0.21 [f]
Ne	0.46 [a]	0.59 [b]	0.65 [a]	0.69 [c]	0.73 [a]	1.0 [c]	0.20 [e] 0.25 [g]	0.51 [f]
Ar	1.9 [a]	3.5 [b]	2.6$_5$ [a]	6.0 [c] 4.1 [d]	3.0$_5$ [a]	6.2 [c] 4.0 [d]	0.65 [e] 0.75 [g]	1.5 [f]
Kr	2.9 [a]	5.1 [b]	4.0 [a]	9.9 [c] 10.6 [b] 10.9 [i]	4.6 [a]	9.4 [c]	1.0 [g]	1.7 [f]
Xe	4.6 [a]	8.7 [b]	6.5 [a]	13.6 [c] 10.7 [d]	7.4 [a]	14.6 [c]	1.45 [g]	3.2 [f]
N_2	-	-	-	4.8 [i] 5.9 [c] 5.9 [k]	-	5.9 [i] 6.1 [c]		

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[a] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. 73, 455 (1959).

[b] E. W. Rothe, P. K. Rol and R. B. Bernstein, Ref. 4d. Based on Q(v) data [14a] (velocity selection).

[c] E. W. Rothe and R. B. Bernstein, Ref. 1c. Thermal beam, scattering chamber. $\bar{Q}$ data. (Mention should also be made of experiments by K. Kodera and T. Tamura (Bull. Chem. Soc. Japan 34, 566 (1961)) on scattering of Na by rare gases. Their results were not interpreted in terms of C, but would yield "low" values, closer to theoretical.)

[d] R. Helbing and H. Pauly, Diplomarbeit (Helbing), Bonn Univ. (1961); also private communication from H. Pauly (June, 1963). Thermal beam, scattering chamber. $\bar{Q}$ data.

[e] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. 75, 607 (1961).

[f] E. W. Rothe, L. L. Marino, R. H. Neynaber, P. K. Rol and S. M. Trujillo, Phys. Rev. 126, 598 (1962). Thermal beam, scattering chamber. $\bar{Q}$ data. Their results for He-He and similar, more extensive data for He-He, -H, -H_2, etc., by H. Harrison (J. Chem. Phys. 37, 1164 (1962)) are not included because of the high relative velocities (i.e., the experiments lie outside of the "low-velocity" regime, defined earlier).

[g] Slater-Kirkwood approximation, from Ref. f.

[h] P. Beck, Ref. 2e. Assume α = 12; from rainbow scattering data. Result is independent of density of crossed beam (scattering gas).

[i] E. W. Rothe, R. H. Neynaber, B. W. Scott, S. M. Trujillo and P. K. Rol, Ref. 14b. Q(v) data (velocity selection).

[j] H. Pauly, Z. f. angew. Physik 9, 600 (1957). Thermal beam, scattering chamber. $\bar{Q}$ data.

[k] R. C. Schoonmaker, J. Phys. Chem. 65, 892 (1961). Q(v) data (velocity selection).

Table 2. Relative Values of C

Entries are ratios: $C/C_{K\text{-}Ar}$

	Theor.[g]	Exp.[c]	Exp.[d]
K - He	0.12	0.088	0.098
- Ne	0.24	0.11_5	-
- Ar	(1.00)	(1.00)	(1.00)
- Kr	1.5	1.6_5	-
- Xe	2.4	2.2_5	2.6
Cs - He	0.13_5	0.14	0.098
- Ne	0.28	0.17	-
- Ar	1.15	1.05	0.98
- Kr	1.7	1.6	
- Xe	2.8	2.4_5	

and E is the collision energy.) This angle corresponds to the trajectory of maximum attraction between the interacting particles. Mason [2a] first pointed out the existence of a singularity and a discontinuity in the angular distribution of scattering at θ_r. He showed that for an Exp (α,6) potential (Eq. 5), θ_r is strongly dependent upon the reduced energy $K \equiv E/\epsilon$ (with a weak dependence on α), so that its location could be used to deduce ϵ. Ford and Wheeler [2b] analyzed the problem semiclassically and showed that this singularity becomes a broad maximum shifted to lower angles, with θ_r located near the inflection point on the high-angle side of the maximum.

The rainbow effect has now been observed for the systems Cs-Hg and K-Hg, [2cd] and similarly for K-Kr and K-HBr [2e]. Fig. 3 shows an example [2d] of a well-resolved rainbow maximum for K-Hg. Fig. 4a shows the observed energy dependence of θ_r for Cs-Hg while Fig. 4b portrays the theoretical dependence of θ_r upon K and α for an Exp (α,6) potential [2a], for a L.-J. (12,6) potential [2d] and for a Morse function [16]. Schlier [17] has recently made similar calculations for the Kihara potential.

By comparing the experimental data $\theta_r(E)$ with the theoretical curves $\theta_r(K)$, the value of ϵ may be ascertained. On the basis of the limited observations thus far available it does not appear possible to distinguish among the potentials, (with the possible exception of the Morse function). In view of the vertical spread of the theoretical curves, i.e. $K(\theta_r)$, associated with different repulsions an accuracy of better than $\pm 5\%$ in ϵ via rainbow scattering is unlikely.

Table 3 lists the values of ϵ thus far determined by this technique, together with two confirmatory values obtained by other methods.

Table 3. Potential Well Depths from Rainbow Scattering

System	$10^{14} \cdot \epsilon$ (erg)	
Cs-Hg	7.7 [2d]	
K-Hg	7.5 [2d]	(cf. 8.3 [18]*)
K-Kr	1.25 [2e]+	(cf. 1.30 [14b,f])
K-HBr	3.85 [2e]+	

* From an analysis of differential scattering with Maxwellian beams.

\+ Assuming $\alpha = 12$.

‡ From an analysis of Q(v), i.e. from the atom-atom impact spectrum.

Beck [2g] has shown that it is possible to estimate the value of r_m (within an uncertainty of perhaps ±20%) from the "shape" of the rainbow maximum, without a measurement of absolute cross sections (or a knowledge of particle densities), thus providing a possible procedure for the estimation of C from angular distribution data alone. Unfortunately the dependence of C upon r_m (i.e., r_m^6) is so strong that an ultimate accuracy in C of better than ±50% is improbable.

Since the rainbow scattering effect is a semiclassical phenomenon it should be widely applicable to many heavy-particle systems. It may become a generally useful technique for the estimation of potential well depths.

4. DeBroglie Interference (Undulations) in the Angular Distribution.

On the basis of considerations presented by Massey and Mohr [1a,19] thirty years ago, oscillatory interference effects are to be expected in the differential elastic scattering cross section when the deBroglie

wavelength λ of the system is of the order of magnitude of the range of the interatomic forces. Observations of interferences in atomic beam scattering by gases were not reported, however, until recently [10a], probably because of severe experimental requirements such as velocity homogeneity, angular resolution, etc. Fig. 5a shows the first of such data [10a], experiments on the angular distribution of the scattering of velocity-selected beams of Li by crossed (thermal) beams of Hg.

Additional experiments [10b] have since been carried out for the systems Li^6- and Li^7- Hg over a wide range of relative velocities, extending the original results. Fig. 5b shows some recent data, plotted with ordinate $\theta^{4/3} \cdot \sin\theta \cdot I(\theta)$ to remove the steep angular dependence and allow for a better estimation of the undulation positions. Theoretical computations (via the partial wave treatment) have been carried out [10b] analogous to those of Refs. 4b and 2f, yielding $I(\theta)$ as a function of the velocity parameter $A = k\sigma$ for various assumed L.-J.(12,6) potential constants to yield best agreement with the observed undulation pattern.

According to the results of Ref. 2f, this pattern (at least at low angles) should be determined almost entirely by the product $s\sigma$ where $s \equiv 2k \sin\frac{\theta}{2}$ is the transverse momentum transfer. Thus in the case of two isotopic systems (1 and 2) the same undulation pattern should obtain if $k_1 = k_2$ (i.e., relative velocities inversely proportional to the reduced masses), in contrast with the classical expectation where the isotopic cross sections would be identical provided $K_1 = K_2$ (i.e. relative velocities inversely proportional to the square root of reduced masses). The experiments [10b] are found to accord with the quantum predictions.

Since the pattern of the angular distribution is governed primarily by the parameter A and is only slightly influenced by the depth of the

well it is possible to obtain an initial estimate of the value of σ (or r_m) by comparing the periodicity of calculated $I(\Theta)$ vs A curves with observed angular distributions at specified k values.

The procedures described above should be applicable to any low reduced mass system at collision energies sufficiently small to allow experimental resolution of the interferences in the angular distribution.

5. Extrema in Q(v)

As mentioned in Sec. 2, undulatory deviations from the monotonic $v^{-2/5}$ dependence of the total cross section (as predicted [2f]) have been observed, for the systems Li-Hg [10b], Li-Xe [13c, 14a], Li-Kr [14a] and K-Kr [14b]. A detailed analysis [4d] of the Li-rare gas cross sections has substantiated the interpretation [2f,g,i] of this effect in terms of a broad maximum in the phase shift vs. angular momentum curve, $\eta(\ell)$, which provides a significant number of non-random phases. The maximum phase η_m increases with decreasing v, and, assuming the attractive well is sufficiently deep, can pass successively through $\pi/2$, π, etc. yielding positive and negative deviations, respectively, from Q_{MM}. These are indexed [2g,j] N = 1, 1.5, etc. (see Fig. 2).

For any assumed potential of the form of Eq. 1, one may evaluate the velocity dependence of η_m and thus the location of the extrema in Q(v). As an illustration consider the L.-J.(12,6) potential; the following condition for the Nth extremum was obtained: [2j]

$$N - \tfrac{3}{8} = 0.301 \frac{\epsilon\sigma}{\hbar v_N}\left[1 - \frac{0.35}{v_N}\left(\frac{\epsilon}{\mu}\right)^{1/2}\right] \qquad (17)$$

where v_N is the velocity of the Nth extremum (valid provided the second term in the brackets is small, e.g. $< 1/2$). Thus the limiting high-velocity

spacing between successive maxima on a 1/v plot is $3.5 \times 10^{-27}/\epsilon\sigma$ (cm^{-1} sec). Graphs of $vQ^{5/2}$ or $C_{app}^{(6)}$ vs. 1/v are termed elastic atom-atom impact spectra. Such a graph (calculated for a L.-J.(12,6) potential) is shown in Fig. 6.

A plot of $N - \frac{3}{8}$ vs v_N^{-1} should pass through the origin (serving to confirm the index assignments); the initial slope yields directly the product $\epsilon\sigma$. Fig. 7 shows the application [4d] of this procedure to the data of Rol and Rothe [14a] for the Li-Xe, Kr, Ar systems.

Considerations based on the shape of $\eta(\ell)$ near η_n indicate that the amplitude of the undulatory deviations in $Q(v)$ decreases with an increase in the parameter B ($\equiv 2\mu\epsilon\sigma^2/\hbar^2$); roughly, the undulation amplitude is given [21] by $U \cong 2.7/\sqrt{B}$, so that for many heavy particle systems (e.g., for $B > 10^4$) the extrema would be undetectable. (However, for a realistic potential well, expected to be somewhat broader than that of an L.-J.(12,6) well of the same ϵ,σ, the calculations of Mueller [4c] indicate a broader maximum in $\eta(\ell)$, and thus a larger undulation amplitude than for the L.-J. well of the same depth.)

From a knowledge of $\epsilon\sigma$ and the absolute cross section $Q(v)$ from which $C^{(6)}$ has been deduced (Sec. 2), one may obtain the ϵ and σ separately; thus, for the L.-J.(12,6) case

$$\sigma = 4^{-1/5}\left[\frac{C^{(6)}}{\epsilon\sigma}\right]^{1/5} \qquad (18)$$

The parameters ϵ,σ thus obtained may be regarded as trial values (e.g., $\pm 10\%$); one then computes $Q(v)$ by partial wave procedures and, after several iterations, converges on the set of potential constants which best fit the observations (see Ref. 4d).

6. Maxima in Elastic Impact Spectra and the Bound States.

A semiclassical analysis [2i,8] has indicated that the extrema in elastic atom-atom impact spectra serve as counters of the vibrational

states of the diatom. One notes that the maximum phase increases monotonically with decreasing velocity, while l_{max} (the l for which η is a maximum) decreases smoothly to zero as $v \to 0$. Thus, as the velocity is decreased, η_m approaches progressively closer to the s-wave phase, which, in turn, increases toward its low-velocity (Levinson's Theorem) limit of $n_o\pi$, where n_o is the number of discrete levels of zero angular momentum (i.e., the number of vibrational states). As mentioned in Sec. 5, a maximum in the impact spectrum is expected each time η_m passes through $(N - \frac{3}{8})\pi$. Thus the total number of such maxima should be n_o.

However, since the assumptions in the semiclassical analysis become progressively less valid as the velocity is decreased, the above result is not rigorous. A re-statement, which should be suitable for application in any practical situation (where measurements are confined to a finite velocity range), is as follows:

The observation of m maxima in the elastic atom-atom impact spectrum implies the existence of at least m vibrational states for the diatom.

Only a few systems have been studied thus far; they have already been mentioned in Sec. 5. As an example, let us consider the Li-Xe [4d] system, for which the lowest observed velocity maximum was indexed N = 3; according to our rule this implies the existence of at least 3 vibrational states for LiXe ($^2\Sigma^+$). Assuming the L.-J.(12,6) potential and using the ϵ, σ parameters evaluated from $Q(v)$ data it is possible to compute the energy levels and total number of bound states by straightforward techniques [20]. One obtains [4d] a capacity $n_o = 8$, suggesting the existence of further undetected maxima in the impact spectrum at lower velocities. Similar consistency (i.e. $m \leq n_o$) has been obtained in all cases studied: neither the number of maxima observed nor the highest index

assigned has exceeded the computed "capacity" of the well.

It is of interest to note that the "level counting" technique described is not dependent on the detailed form of the potential assumed and may well have considerable generality (i.e. extension to molecular and/or charged particle systems, etc.). Its usefulness will, of course, be limited by the experimental difficulty of resolving the maxima and by the possible loss of detail when inelastic processes are concurrent.

Conclusions

The inverse sixth-power radial dependence of the long-range attractive potential appears to be well established by experiments of several different types. However, the C constants derived from the scattering measurements are higher than the theoretical values. It is suggested that an absolute experimental determination of a "reference cross section" is urgently needed.

Although the problem of deducing the complete potential function from scattering measurements is still formidable, it is now becoming possible to evaluate the separate constants in a two-parameter representation of the potential. For example, the energy dependence of the rainbow effect in $I(\theta)$ has yielded ϵ within ± 5-10%, while the extrema-locations in $Q(v)$ have yielded the product ϵr_m within ± 3-4%. From absolute total cross sections (thus C values) and a knowledge of ϵ or the ϵr_m product, r_m may be obtained within ± 10-20%. In addition, less extensive evidence suggests the possiblity of estimating r_m directly from rainbow scattering, from the quantum effect (undulations) in $I(\theta)$, and from absolute values of the (classical) differential cross section. Further work in each of these areas is desirable.

For a given interatomic potential function it is a straightforward task to compute the "capacity" of the well for bound states. It appears possible to establish an experimental lower limit on the number of vibrational levels by counting the maxima in the atom-atom impact spectrum. This result can then be compared for consistency with the capacity predicted from the potential constants characterizing the well. Since the bound-state counting procedure appears to be independent of the potential assumed, it may have general applicability.

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Legends for Figures

1. Log-log plots [2d] of (a) observed angular distribution of intensity (lab. system) for scattering of thermal K beam by crossed thermal Hg beam; (b)-(d) differential cross sections vs. c.m. angle; with velocity selection. Solid line: slope = -7/3.

2. Log-log plot [2g] of the velocity dependence of the total cross section calculated for scattering by a L.-J.(12,6) potential with a particular set of parameters. Here $B \equiv 2\mu\epsilon\sigma^2/\hbar^2 = 125$, $A \equiv k\sigma$, $Q^* \equiv Q/\pi\sigma^2$ and $D \equiv B/A = 2\epsilon\sigma/\hbar v$.

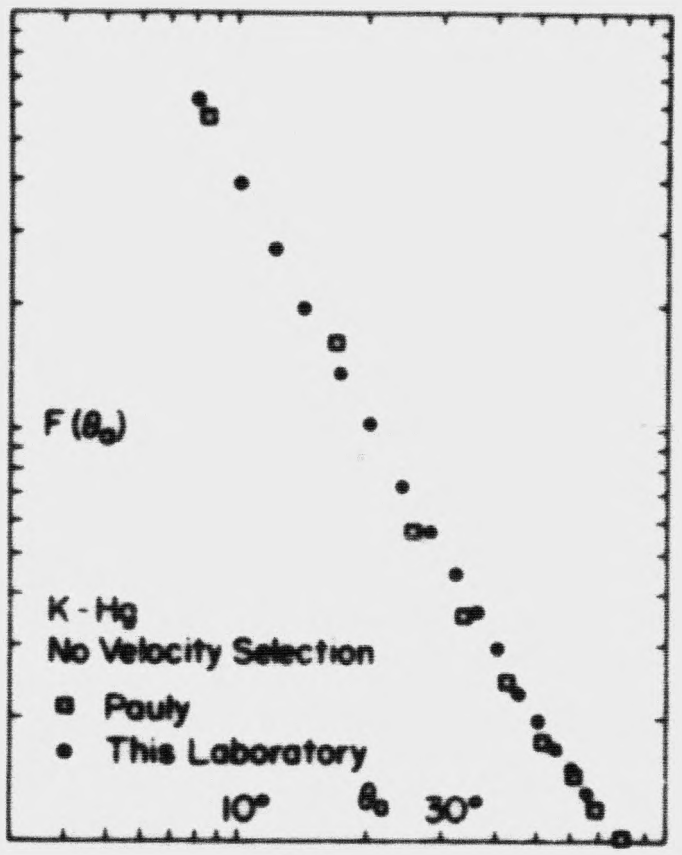
3. Observed data [2d] (linear plot of scattered intensity vs. lab. angle) showing the detail of a rainbow maximum. K-Hg, $\bar{v}_r = 1.0 \times 10^5$ cm sec^{-1}.

4. (a) Observed energy dependence [2d] of Θ_r for Cs-Hg; (b) theoretical dependence of Θ_r upon K for the following potentials: Exp (α,6) L.-J.(12,6) and Morse (with a = 12.77) [1e].

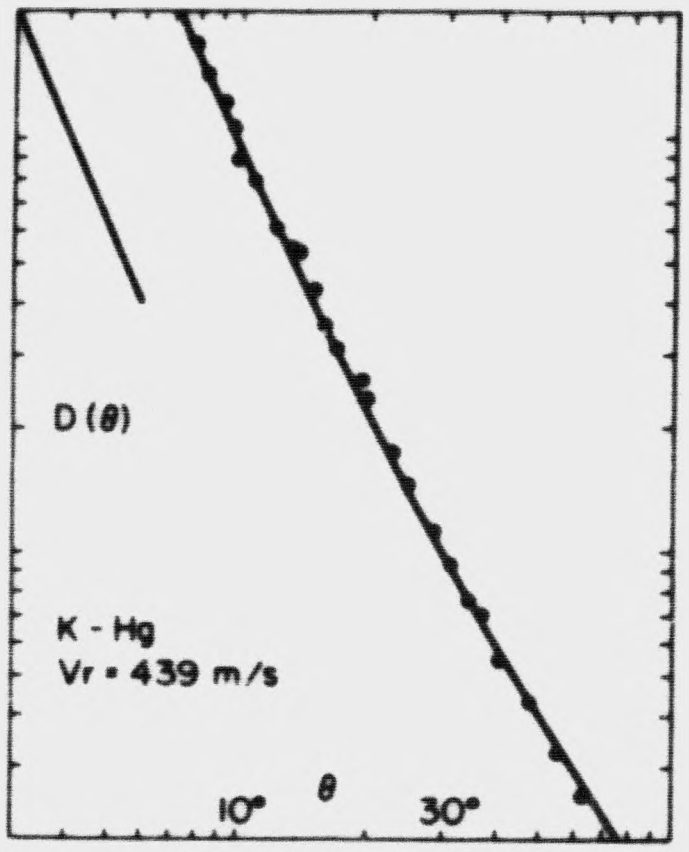
5. (a) Observed angular dependence [10a] of the scattering of Li by Hg at several values of $\bar{v}_r$; (b) recent data [10b] showing the presentation which removes the steep angular dependence (for estimation of extrema-angles).

6. Upper curve: theoretical form of atom-atom impact spectrum (the ordinate and abscissa are proportional to $v^{2/5} \cdot Q(v)$ and $1/v$, respectively) calculated [4d] via partial-wave (PW) procedures for the L.-J.(12,6) potential, with B = 650; vertical marks predicted by Eq. 17. Lower curve: extremum index N vs. D (proportional to 1/v).

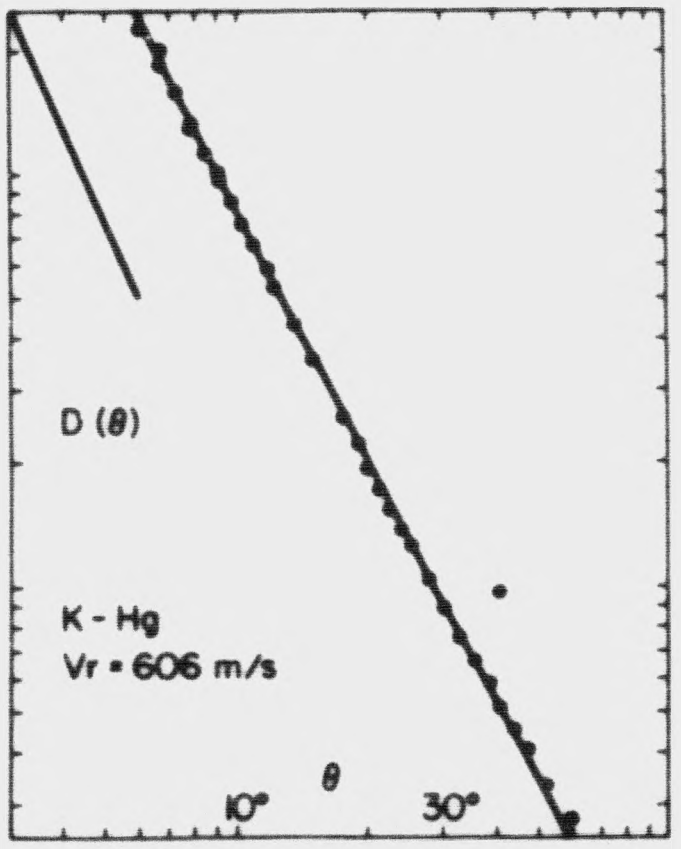
7. Experimental results [4a,4d] for Li-rare gas systems: N vs $1/v_N$. The brackets indicate the uncertainty in locating the extrema. Values of shown are those obtained from the limiting slopes as $1/v \to 0$. Crosses show the values predicted using finally chosen parameters: $\epsilon\sigma$ = 9.47, 6.09, 3.82 (10^{-22} erg cm) for Li-Xe, Kr, and Ar, respectively.


F(θ_lab)
K - Hg
No Velocity Selection
Pauly
This Laboratory
10°
θ_lab
30°

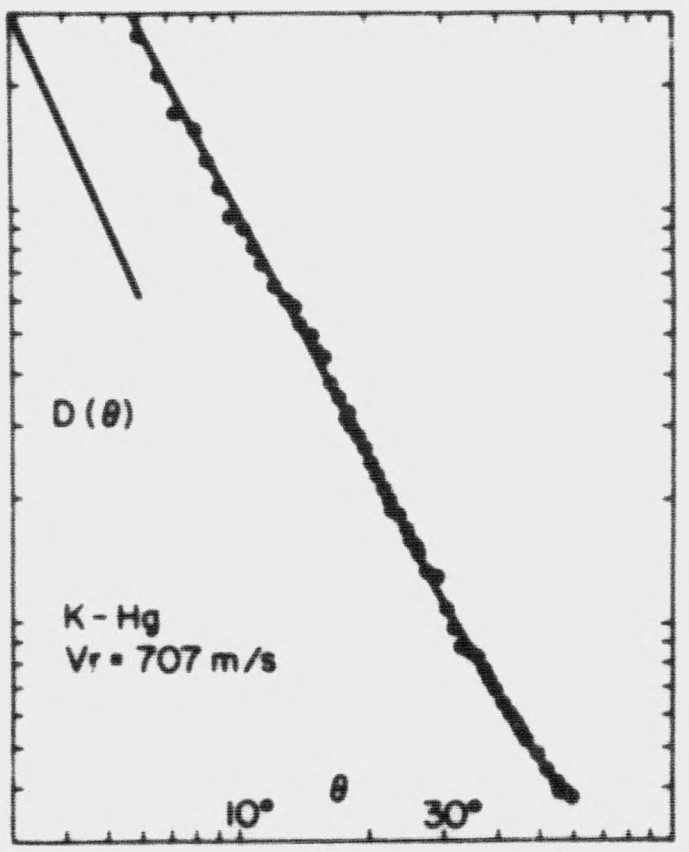
(a)


D (θ)
K - Hg
Vr = 439 m/s
10°
θ
30°

(b)


D (θ)
K - Hg
Vr = 606 m/s
10°
θ
30°

(c)


D (θ)
K - Hg
Vr = 707 m/s
10°
θ
30°

(d)

Fig. 1

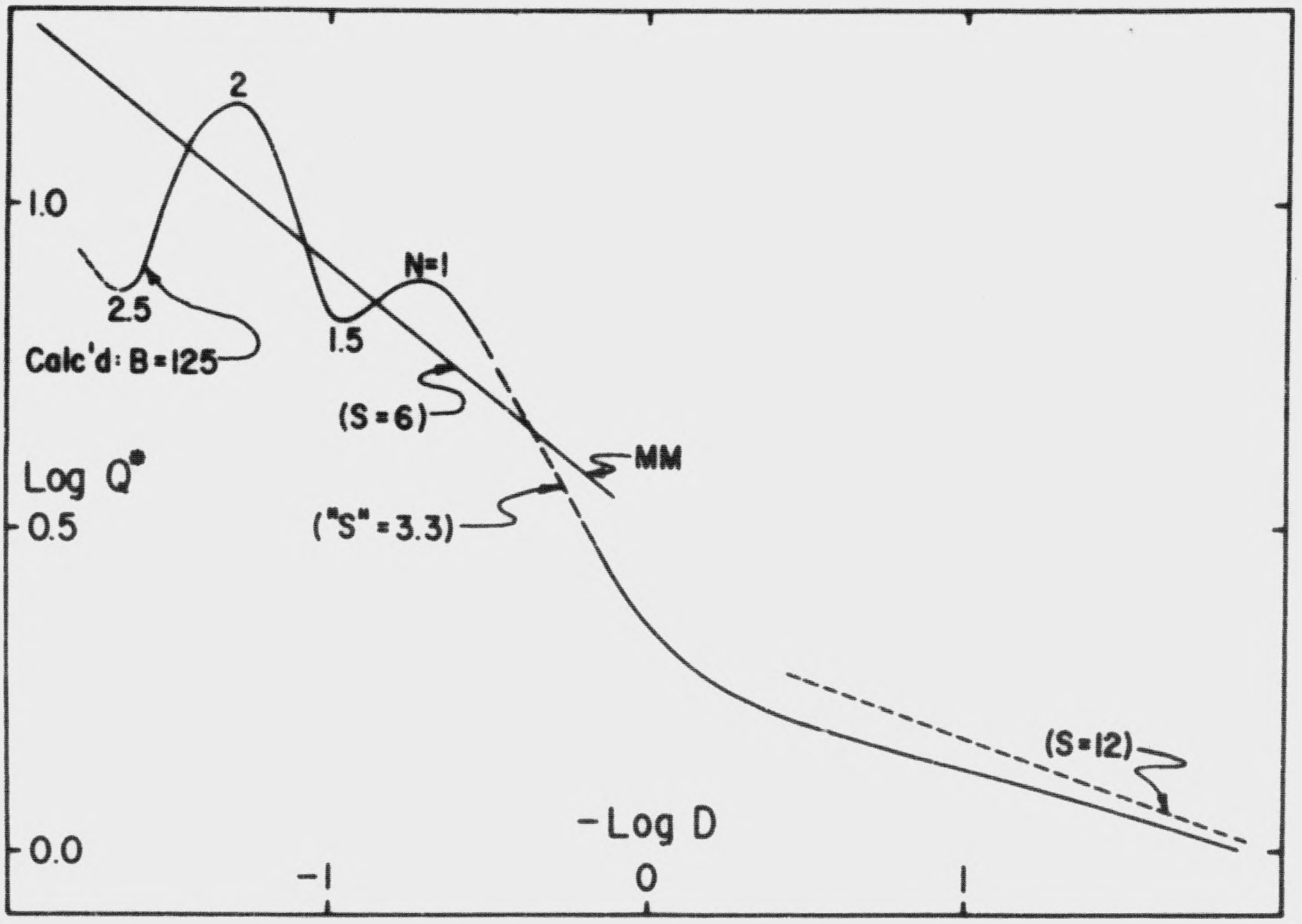


Fig. 2

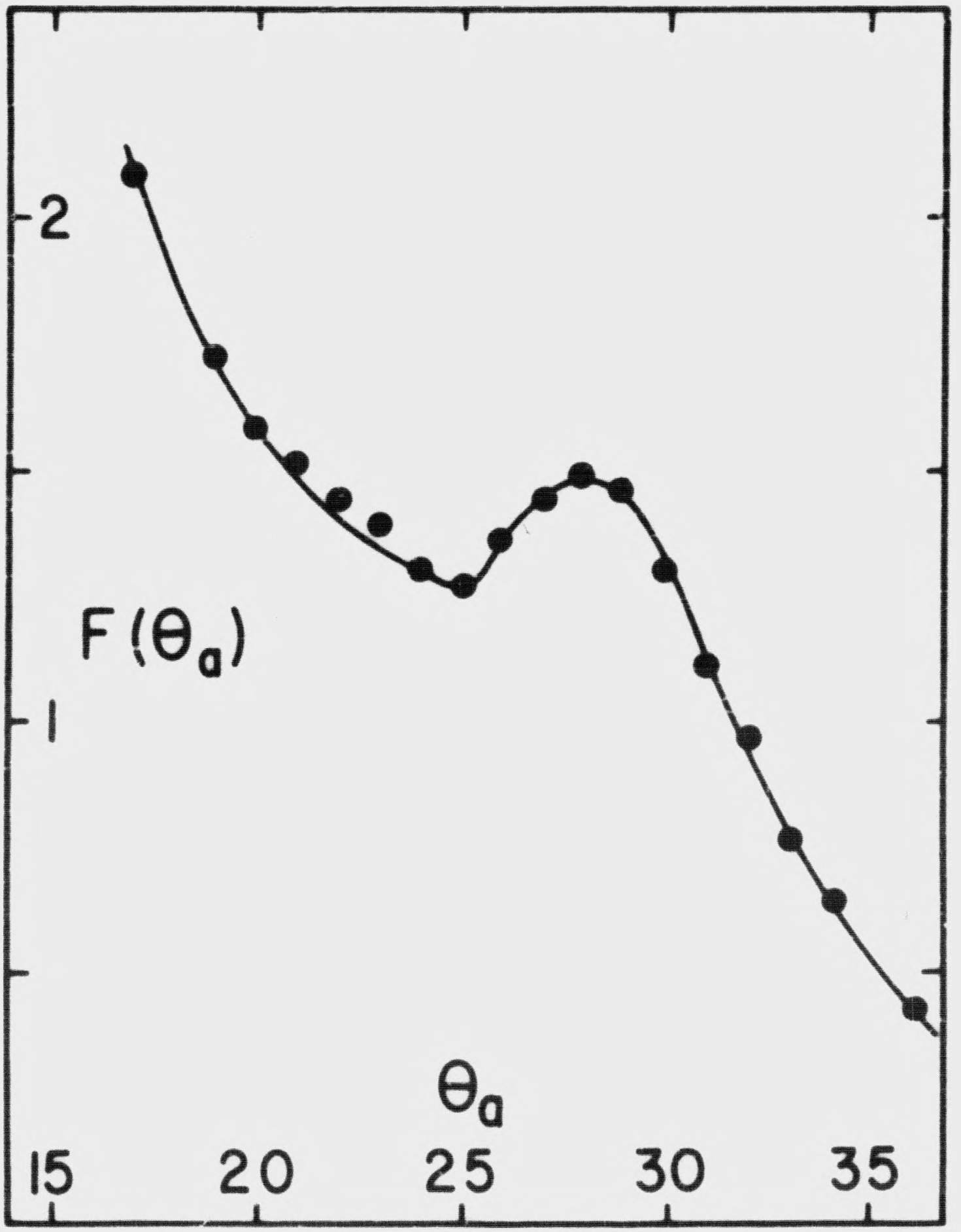


Fig. 3

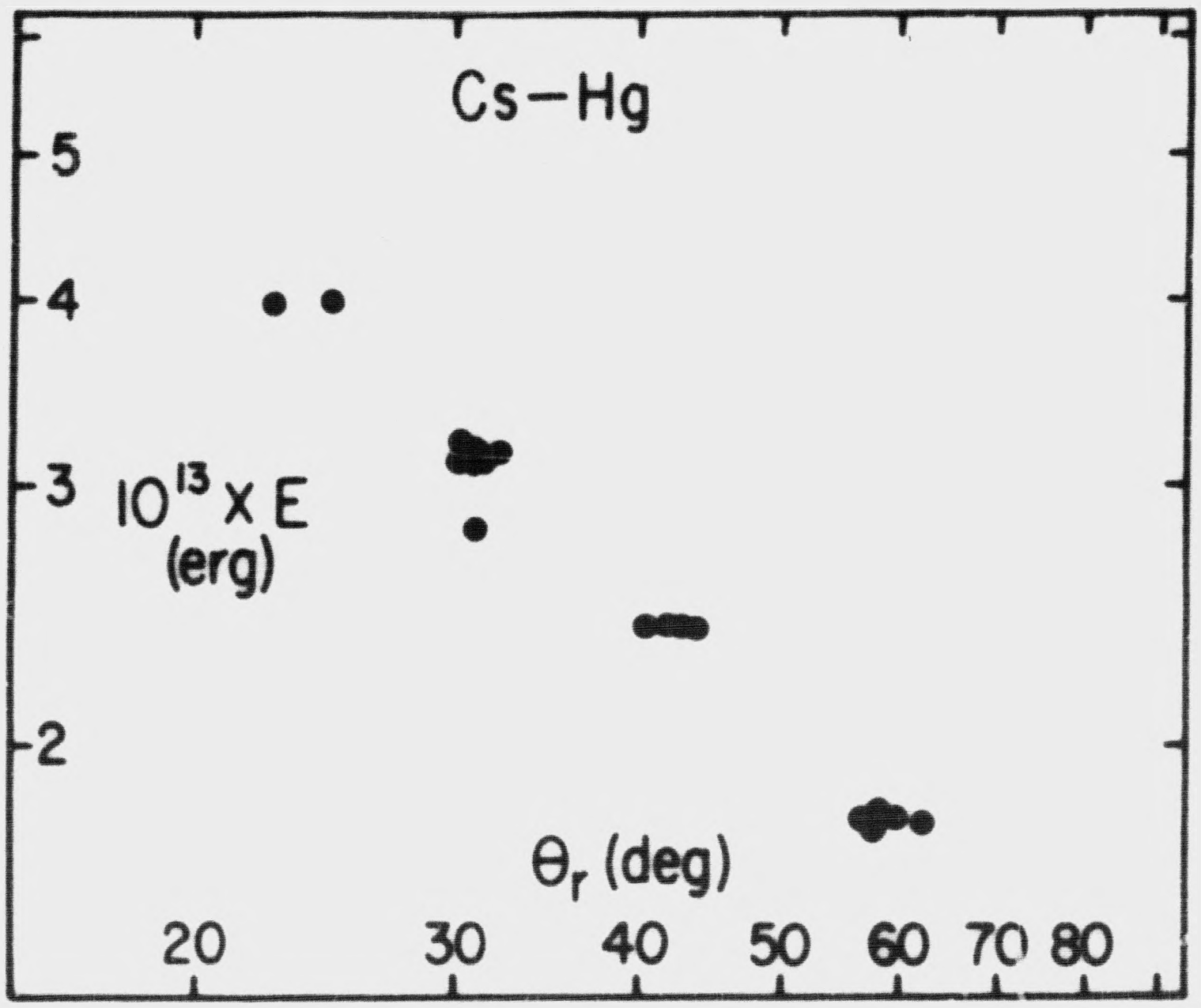


Fig. 4a

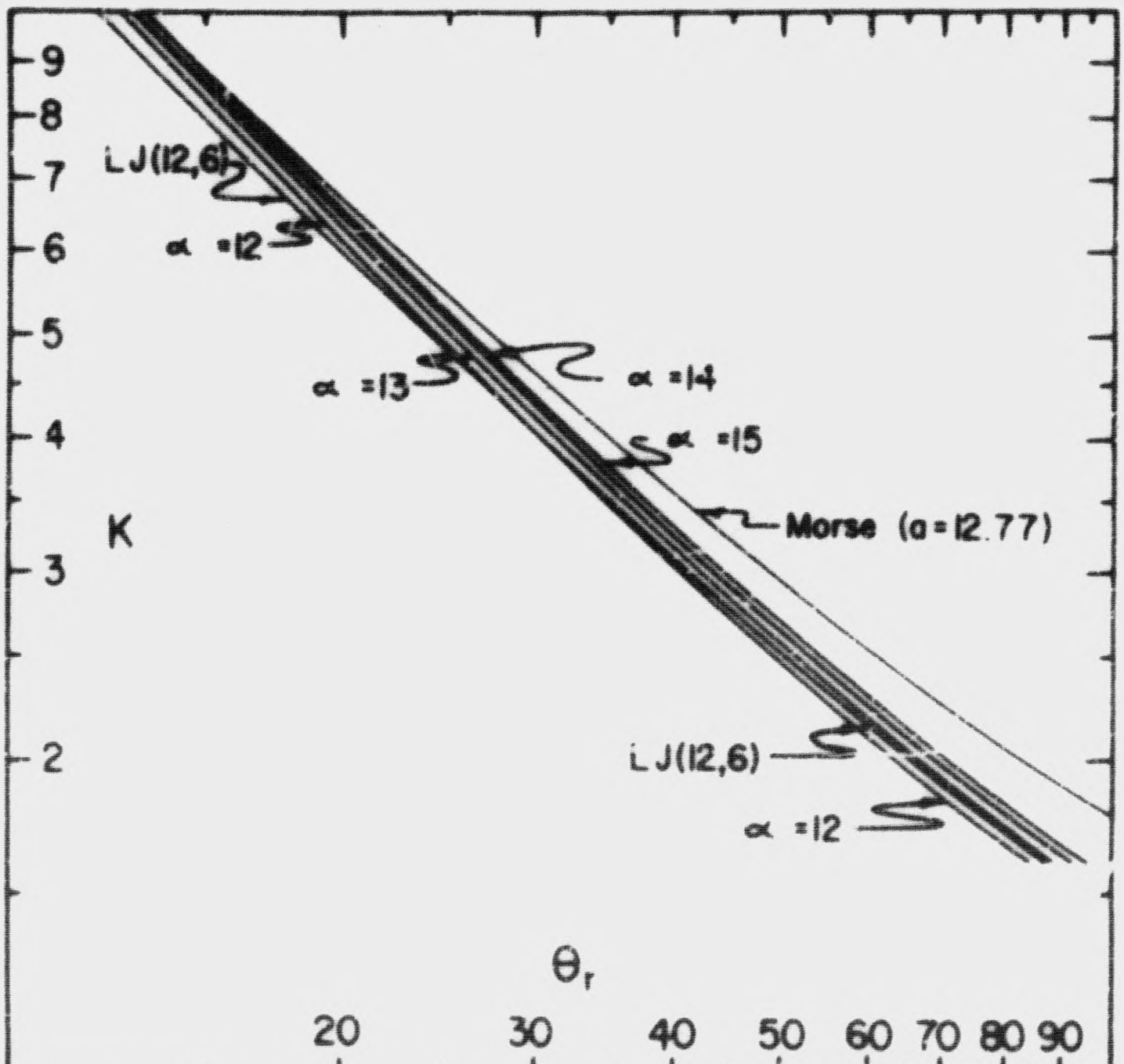

9
8
7
6
5
4
3
2
K
LJ(12,6)
α =12
α =13
α =14
α =15
Morse (a=12.77)
LJ(12,6)
α =12
θr
20
30
40
50
60
70
80
90

Fig. 4b

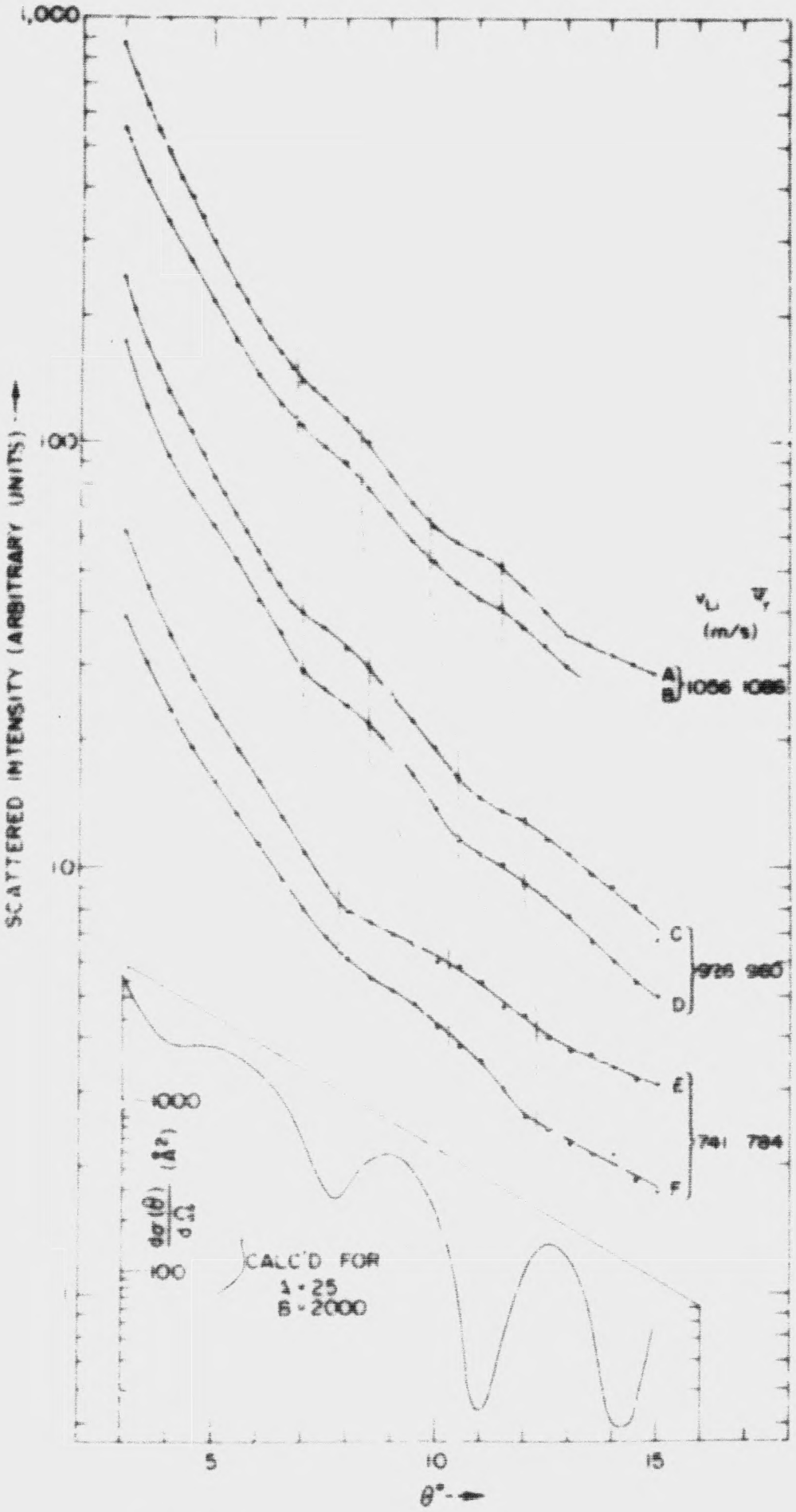

1,000
100
10
SCATTERED INTENSITY (ARBITRARY UNITS) →
A
B
1056
1086
C
D
926
980
E
F
741
784
1000
100
CALC'D FOR
A = 25
B = 2000
5
10
15
θ° →

Fig. 5a

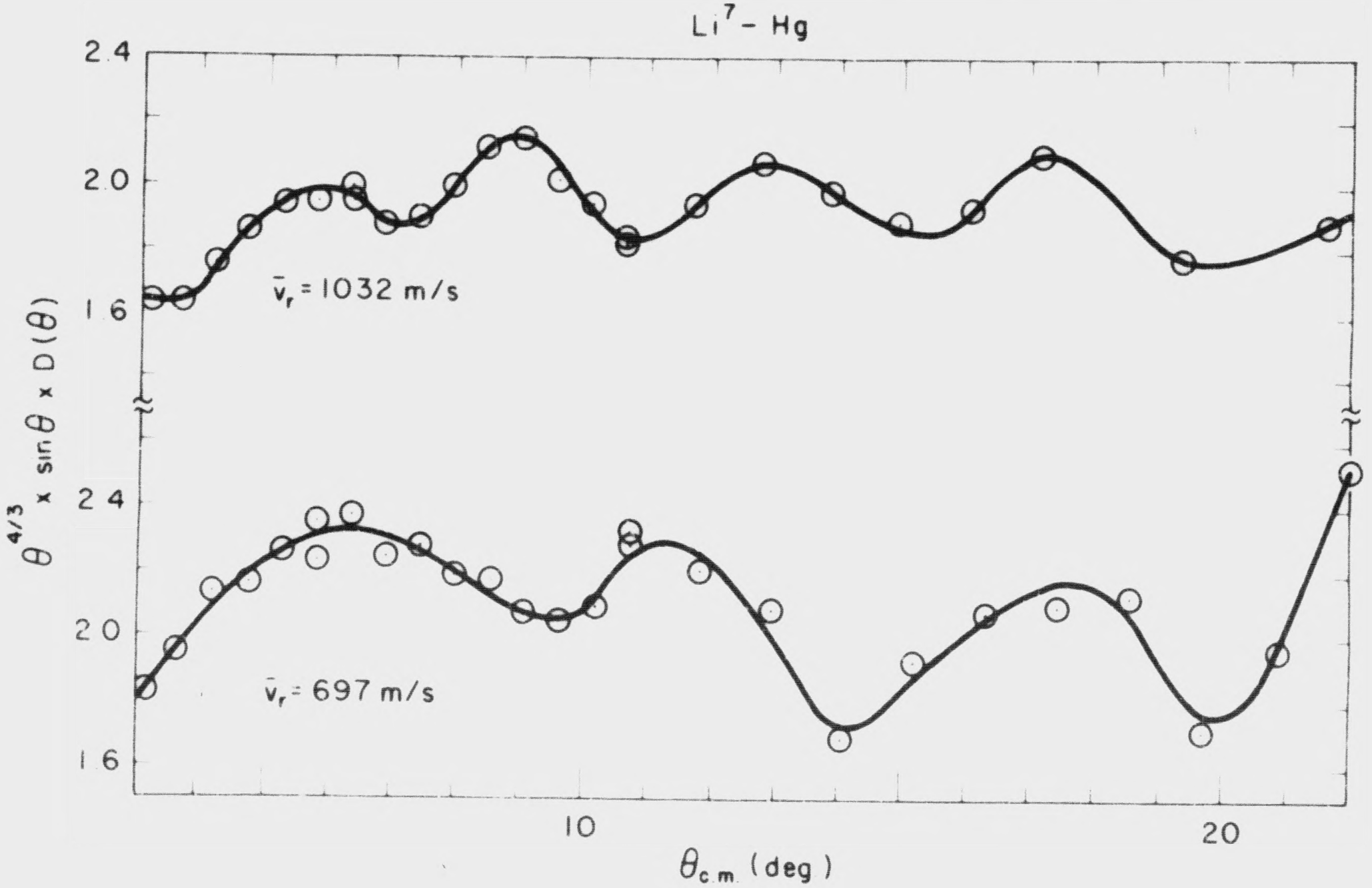

Li⁷ - Hg
2.4
2.0
1.6
$\bar{v}_r$ = 1032 m/s
$\theta^{4/3} \times \sin\theta \times D(\theta)$
2 4
2 0
1 6
$\bar{v}_r$ = 697 m/s
10
20
$\theta_{c.m.}$ (deg)

Fig. 5b

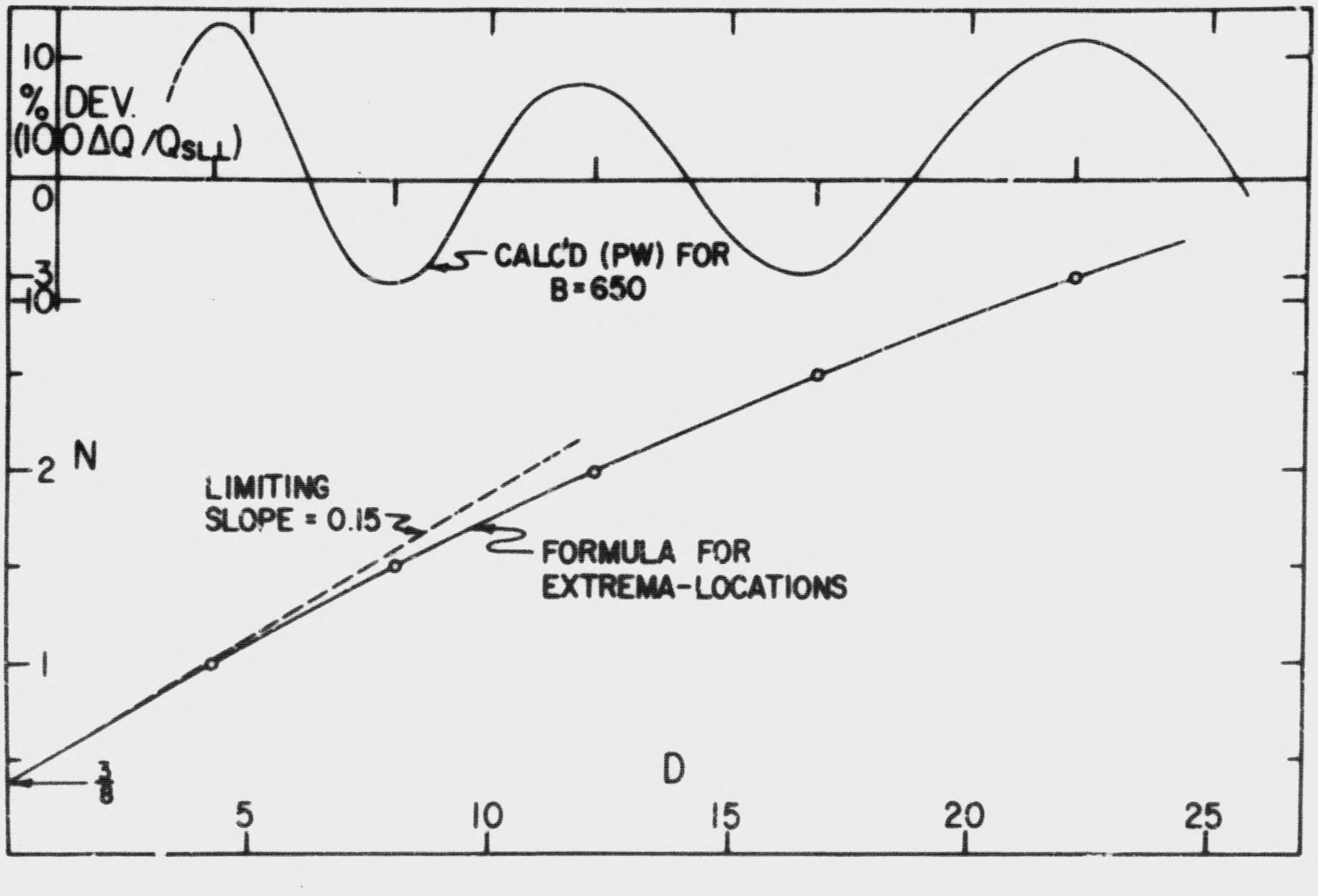

10
% DEV.
(100 ΔQ / Q_SLL)
0
3/10
CALC'D (PW) FOR
B=650
N
2
LIMITING
SLOPE = 0.15
FORMULA FOR
EXTREMA-LOCATIONS
1
3/8
D
5
10
15
20
25

Fig. 6

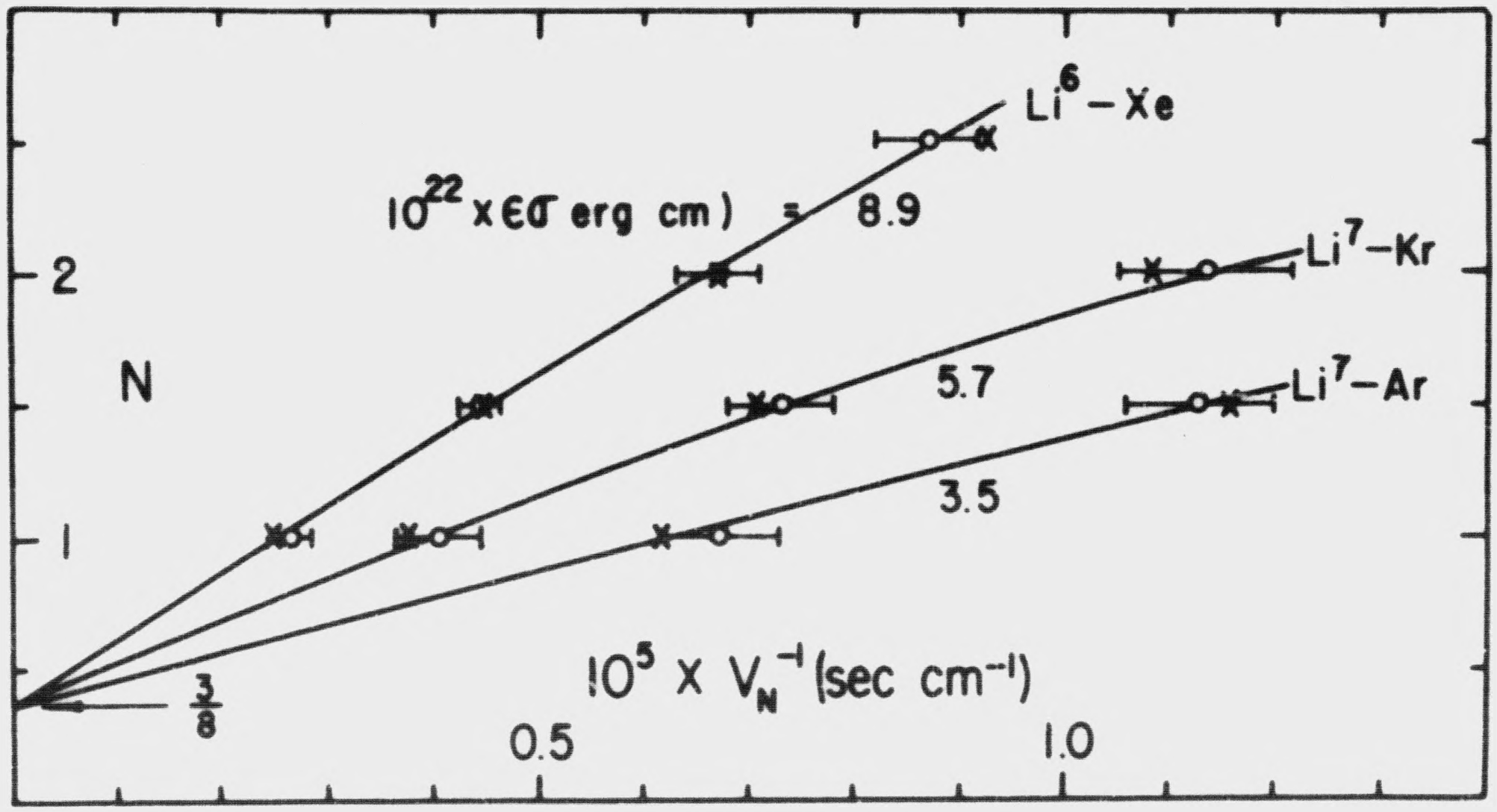

6
$Li^6 - Xe$
$10^{22} \times \epsilon\sigma$ erg cm) = 8.9
2
N
$Li^7 - Kr$
5.7
$Li^7 - Ar$
3.5
1
$10^5 \times V_N^{-1}$ (sec cm^{-1})
$\frac{3}{8}$
0.5
1.0

Fig. 7

END