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A Method of Correction of the Angular Resolution for Determination of Absolute Total Cross Sections Using Molecular Beams

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A general method is given for the correction of angular resolution for the case in which primary beams have a monochromatic velocity and the target gases in the scattering chamber have Maxwellian distribution. In the center-of-mass system the differential cross section for small angles are expressed by three analytical formulas. An apparent differential cross section in the laboratory system is given by averaging contributing differential cross sections in the center-of-mass system. For correction of the angular resolution, the detection probability R is defined for rectangular beams and detector. Using the apparent differential cross section with R-function and beam profile, we can determine the correction factor $\Delta Q_{\mathrm{eff}}(v_1)/Q_{\mathrm{eff}}(v_1)$. The expression of angular resolution has been applied to previous experimental data.

In a previous study for the determination of absolute total cross sections using molecular beams,[1] sources of error were pointed out and corrected. However, Busch's correction[2] used for the angular resolution of the beam apparatus is not complete, because the formula is only applicable to the case $v_1 \gg v_{\mathrm{kw}}$ (*i.e.*, the velocity of the primary beam is much greater than the most probable velocity of the target gases). This is not always the case for experiments in thermal energy range. A general method applicable for slow primary beams is discussed in this paper. For the sake of simplicity, it is assumed that the primary beams have a monochromatic velocity and the target gases in the scattering chamber have Maxwellian distribution.

1. Differential Cross Section in the Center-of-mass System

In the thermal energy range, the total scattering cross section and the differential cross section for small angles are mainly determined by the van der Waals force. The van der Waals potential is given by

$$V(r) = -C/r^s. \tag{1}$$

The van der Waals constant C is related to the absolute total cross section Q by the Schiff-Landau-Lifshitz approximation as follows.

$$Q = p(s)\left[\frac{C}{\hbar g}\right]^{2/(s-1)}, \tag{2}$$

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1) I. Kusunoki, This Bulletin, **44**, 2067 (1971).

2) F. Busch, *Z. Phys.*, **193**, 412 (1966).

where

$$p(s) = \frac{\pi^2[2f(s)]^{2/(s-1)}}{\sin\left(\frac{\pi}{2}-1\right)\Gamma\left(\frac{2}{s}-1\right)}.$$

In this case the differential cross section in the classical theory is given by[3)]

$$\sigma_c(\theta) = \frac{(s-1)^{2/s}}{s}\left(\frac{2f(s)C}{\mu g^2}\right)^{2/s}\theta^{-2(s+1)/s}, \tag{3}$$

where

$$f(s) = \frac{\sqrt{\pi}\,\Gamma\left(\frac{s-1}{2}\right)}{2\Gamma\left(\frac{s}{2}\right)},$$

μ is the reduced mass, and g the relative velocity. According to Mason *et al.*,[4)] this formula is only applicable above the critical angle,

$$\theta_c \approx \left[\frac{\pi^2\hbar^2}{2\mu}\right]^{s/2s-2}[(s-1)f(s)C]^{-1/(s-1)}E^{-(s-2)/(2s-2)}, \tag{5}$$

where

$$E = \frac{1}{2}\mu g^2. \tag{6}$$

For $s=6$ the angle corresponds to

$$\theta_c \simeq 4.445\theta^*. \tag{6}$$

where

$$\theta^* = \frac{1}{k}\sqrt{\frac{\pi}{Q}} \tag{7}$$

and $k=\mu g/\hbar$.

The differential cross section for very small angle can be approximated by a semi-classical theory; Mason *et al.* put it into the following compact exponential form.

$$\sigma_s(\theta) = \left[\frac{kQ}{4\pi}\right]^2\left[1+\tan^2\left(\frac{\pi}{s-1}\right)\right]\exp\left[-\frac{g(s)k^2Q\theta^2}{8\pi}\right], \tag{8}$$

where

$$g(s) = \left[\Gamma\left(\frac{2}{s-1}\right)\right]^2\left[2\pi\Gamma\left(\frac{4}{s-1}\right)\right]^{-1}\tan\left(\frac{2\pi}{s-1}\right), \; s>5 \tag{9}$$

However, Eq. (8) is only applicable for angles such as

$$\theta < [\pi^2 g(s)/2]^{-1/2}\theta_c. \tag{10}$$

For $s=6$ this is reduced to $\theta<0.31\theta_c(=1.38\theta^*)$.

From the above discussion the differential cross sections for the angular range $\theta_c>\theta>0.31\theta_c$ cannot be obtained. But in Busch's paper both Eqs. (3) and (8) are used to express the differential cross section over the whole small angular range, connecting the two equations at the larger one ($2.817\theta^*$) of the angles where they intersect. It seems that the differential cross section is overestimated in the angular range $2.817\theta^*>\theta>1.38\theta^*$. (See Fig. 1). We have used a modified classical cross section given by Mason *et al.* in the angles smaller than θ_c:

$$\sigma_m(\theta) = \sigma_c(\theta)[1+(2kb\theta)^{-2}+\cdots]$$

$$\simeq \sigma_c(\theta)\left[1+\frac{\pi}{2k^2\theta^2Q}\right]. \tag{11}$$

3) E. W. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Company, Inc., New York (1938).

4) E. A. Mason, J. T. Vanderslice, and C. J. G. Raw, *J. Chem. Phys.*, **40**, 2153 (1964).

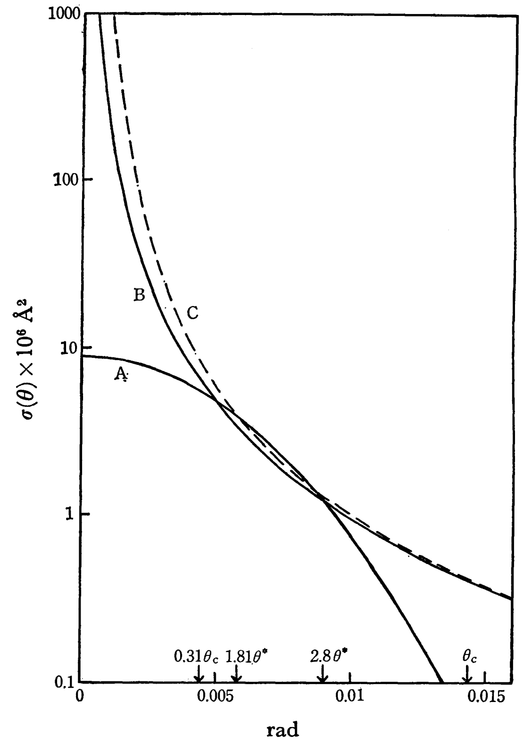

Fig. 1. Differential cross section for K–Ar at g=800 m/s. Curve A is the small-angle quantum result according to Eq. (8), Curve B is the classical result according to Eq. (5), and Curve C (dashed curve) the almost classical result according to Eq. (11).

To connect Eqs. (11) and (8) smoothly, the angles of the cross points of the two equations were estimated by a computer under the experimental conditions given previously.[1)] The inner angle of the cross points was always obtained near $\theta=1.81\theta^*$. The differential cross sections for small-angle scattering are then expressed by the following three formulas.

$$\begin{aligned} &\theta>4.445\theta^* && \sigma(\theta)=\sigma_c(\theta)\\ &4.445\theta^*>\theta>1.81\theta^* && \sigma(\theta)=\sigma_m(\theta)\\ &1.81\theta^*>\theta && \sigma(\theta)=\sigma_s(\theta). \end{aligned} \tag{12}$$

By the use of these differential cross sections, the curve of $\sigma(\theta)$ turns out to be smoothen as shown in Fig. 1.

2. Differential Cross Section in the Laboratory System

For the correction of the angular resolution in the laboratory (LAB) system, it is necessary to convert the differential cross sections from the center-of-mass (c.m.) system into the LAB system. Figure 2 shows the geometrical relationship for the transformation. The notations in Fig. 2 are as follows.

$\boldsymbol{v}_i$, the velocity vector of the beam particle before the collision in the LAB system.

$\boldsymbol{v}_k$, the velocity vector of the target particle before the collision in the LAB system.

$\boldsymbol{u}_i$, the velocity vector of the beam particle before the collision in the c.m. system.

(Primed quantities such as $\boldsymbol{v}_i'$, $\boldsymbol{v}_k'$, and $\boldsymbol{u}_i'$ designate "after the collision".)

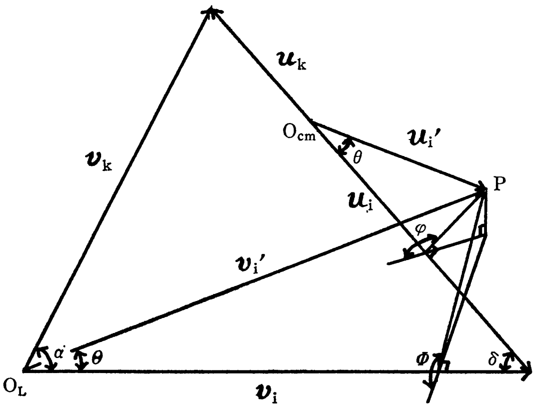

Fig. 2. The definition of quantities for the transformation from the center-of-mass system to the laboratory system.

$\boldsymbol{g}$, the relative velocity vector before the collision.
α, the angle between $\boldsymbol{v}_i$ and $\boldsymbol{v}_k$.
δ, the angle between $\boldsymbol{g}$ and $\boldsymbol{v}_i$.
θ, the deflection angle of the beam particle in the c.m. system.
Θ, the deflection angle of the beam particle in the LAB system.
φ, the azimuthal angle of the vector of $\boldsymbol{u}_i'$ in the c.m. system.
Φ, the azimuthal angle of the vector of $\boldsymbol{v}_i'$ in the LAB system.

The magnitude of the relative velocity is then given by

$$g = \sqrt{v_i^2 + v_k^2 - 2v_i v_k \cos\alpha}, \tag{13}$$

and the angle δ by

$$\delta = \sin^{-1}\frac{v_k \sin\alpha}{\sqrt{v_i^2+v_k^2-2v_iv_k\cos\alpha}}. \tag{14}$$

Therefore, both values of g and δ are determined by a set of (v_i, v_k, α).

For elastic collisions it is evident that a small angle in the c.m. system is transformed into a small angle in the LAB system. According to Helbing,[5] the transformation formulas between the c.m. system and the LAB system can be approximated for small deflection angles as follows.

$$\Theta = \theta\left(\frac{\mu g}{m_i v_i}\right)(1-\sin^2\delta\cos^2\varphi)^{1/2}, \tag{15}$$

$$\tan\Phi = \tan|\varphi|/\cos\delta, \quad \varphi \gtrless 0 \rightleftarrows \Phi \gtrless 0 \tag{16}$$

$$\frac{d\omega}{d\Omega} = \left(\frac{m_i v_i}{\mu g}\right)^2 |\cos\delta|^{-1}. \tag{17}$$

The differential cross section in the LAB system can then be given by

$$\sigma(\Theta, \Phi) = \sigma(\theta, \varphi)\frac{d\omega}{d\Omega}, \tag{18}$$

where θ is determined by a set of $(v_i, m_i, v_k, m_k, \alpha, \varphi, \Theta)$. The total cross section $Q(g)$ in Eqs. (8) and (11) is related to $Q(v_i)$ by Eq. (2):

$$Q(g) = Q(v_i)\left(\frac{v_i}{g}\right)^{2/s-1}. \tag{19}$$

If the target gas follows the Maxwellian distribution $f(v_k)$ and isotropic spatial distribution, the particles scattered into a laboratory angle Θ are originated from those scattered at various angles in the c.m. system. In such a case, the apparent differential cross section for small-angle scattering in the LAB system is given by

$$\sigma_{ap}(v_i, \Theta) = \frac{1}{4\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{2\pi}\sigma(\theta)\frac{d\omega}{d\Omega}f(v_k)\sin\alpha\, d\varphi\, dv_k\, d\alpha. \tag{20}$$

If the apparent differential cross section multiplied by $2\pi\sin\Theta$ is integrated from 0 to π, the effective total cross section averaged by the thermal motion of the target gas will be obtained:

$$Q_{eff}(v_i) = 2\pi\int_0^{\pi}\sigma_{ap}(v_i, \Theta)\sin\Theta\, d\Theta \tag{21}$$

3. Correction of the Angular Resolution

Beam apparatus always have finite angular resolution for detection of scattering events. If the cross section of the beam is a very small circle and that of the detector a circle of finite radius, the apparatus will have a constant resolving power γ at a distance from a scattering point to the detector. In this case, the correction value of the total cross section for the beam deflected into small angles is given by

$$\Delta Q_{eff}(v_i) = 2\pi\int_0^{\gamma}\sigma_{ap}(v_i, \Theta)\sin\Theta\, d\Theta. \tag{22}$$

In general, however, cross sections of the beam and the detector are narrow rectangles.[1] In such a case, the angular resolving power is not constant, but depends on the position in the plane of the detector and the scattering point in the scattering region. Let us consider the dependence of resolution on the position of a beam particle in a scattering plane and on the position of detection of the particle. (See Fig. 3.)

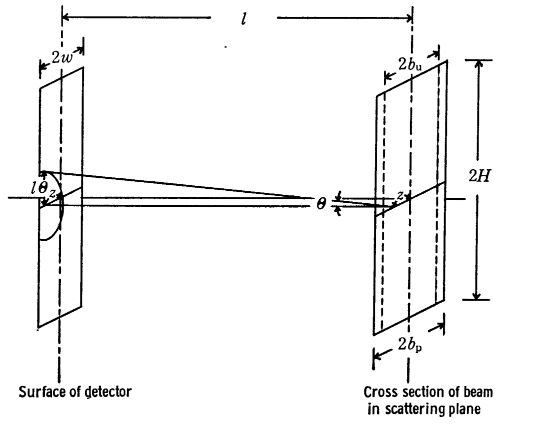

Fig. 3. Geometrical parameters for the correction of angular resolution.

It is assumed herewith that the width of the beam is much smaller than its height, the intensity distribution in the beam is uniform along its height and the detector has infinite length. The intensity distribution along its width is determined by the geometrical relationship of the beam apparatus. The widths of the umbra and penumbra in the trapezoidal profile are given by

$$2b_u = \left\{w_c - (w_s - w_c)\frac{l_{cd}}{l_{sc}}\right\}, \tag{23}$$

5) R. Helbing, *J. Chem. Phys.*, **48**, 472 (1968).

and

$$2b_{\rm p} = \left\{w_{\rm c} + (w_{\rm s}+w_{\rm c})\frac{l_{\rm cd}}{l_{\rm sc}}\right\}, \tag{24}$$

respectively, where w_c and w_s are the widths of the collimating slit and source slit, respectively, l_{cd} is the distance from the collimating slit to the detector, and l_{sc} is the distance from the source slit to the collimating slit. If the central line of the beam along its height coincides with that of the detector, the intensity of the unscattered primary beam depends on the horizontal distance z from the vertical central line, and is given by

$$\begin{aligned} &z < b_{\rm u} && i_0(z) = i_{\rm m}, \\ &b_{\rm u} < z < b_{\rm p} && i_0(z) = \frac{b_{\rm p}-z}{b_{\rm p}-b_{\rm u}} i_{\rm m}, \\ &b_{\rm p} < z && i_0(z) = 0, \end{aligned} \tag{25}$$

where i_m is the intensity per unit width in the umbra. The intensity of the unscattered beam measured by the detector is then given by

$$I_0 = \int_{-w}^{w} i_0(z)\,{\rm d}z, \tag{26}$$

where $2w$ is the width of the detector.

Consider a particle scattered from a point at a distance l from the plane of the detector and at a distance z from the vertical central line of the beam (Fig. 3). If the trajectories of the incident particles at the scattering plane are sufficiently parallel to each other, a part of the beam scattered through an angle Θ and falling on the detector is given by

$$2\pi n i(z) R(z, l, \Theta)\sigma_{\rm ap}(\Theta)\sin\Theta{\rm d}\Theta, \tag{27}$$

where n is the density of the scattering gas, $i(z)$ is the beam intensity at the scattering point, and $R(z,l,\Theta)$ is the portion of the circumference of the circular cone of the scattered beam intercepted by the detector. When the radius of the base of the circular cone at the detector is r, we have $\Theta \equiv \tan^{-1} r/l \simeq r/l$ for small angle scattering. Thus the R-function is given by the following expressions.

for $z \geq w$

$$\begin{cases} z - w \geq l\Theta & R(z, l, \Theta) = 0, \\ z + w \geq l\Theta \geq z - w & R(z, l, \Theta) = \dfrac{1}{\pi}\cos^{-1}\left(\dfrac{z-w}{l\Theta}\right), \\ l\Theta \geq z + w & R(z, l, \Theta) = \dfrac{1}{\pi}\left\{\cos^{-1}\left(\dfrac{z-w}{l\Theta}\right) - \cos^{-1}\left(\dfrac{z+w}{l\Theta}\right)\right\}, \\ l\Theta \gg z + w & R(z, l, \Theta) \longrightarrow \dfrac{2w}{\pi l\Theta}, \end{cases} \tag{28}$$

for $z < w$

$$\begin{cases} l\Theta \leq w - z & R(z, l, \Theta) = 1, \\ z + w \geq l\Theta > w - z & R(z, l, \Theta) = 1 - \dfrac{1}{\pi}\cos^{-1}\left(\dfrac{w-z}{l\Theta}\right), \\ l\Theta > w + z & R(z, l, \Theta) = 1 - \dfrac{1}{\pi}\cos^{-1}\left(\dfrac{w-z}{l\Theta}\right) - \dfrac{1}{\pi}\cos^{-1}\left(\dfrac{w+z}{l\Theta}\right), \\ l\Theta \gg w + z & R(z, l, \Theta) \longrightarrow \dfrac{2w}{\pi l\Theta}. \end{cases} \tag{29}$$

for special case of $z=0$

$$\begin{cases} l\Theta \leq w & R(l, \Theta) = 1, \\ l\Theta > w & R(l, \Theta) = 1 - \dfrac{2}{\pi}\cos^{-1}\left(\dfrac{w}{l\Theta}\right), \\ l\Theta \gg w & R(l, \Theta) \longrightarrow \dfrac{2w}{\pi l\Theta}. \end{cases} \tag{30}$$

The parameter z takes values smaller than b_p. Thus when Θ is much larger than b_p/l and w/l, the R-function can be approximated by $2w/\pi l\Theta$ which is independent of z.

If the width of the beam is much smaller than that of the detector, the correction of the effective total cross section is given by

$$\begin{aligned} \Delta Q_{\rm eff}(v_{\rm i}) &= 2\pi\int_0^{\pi} R(\Theta)\sigma_{\rm ap}(v_{\rm i}, \Theta)\sin\Theta{\rm d}\Theta \\ &\simeq 2\pi\int_0^{\Theta'} \sigma_{\rm ap}(v_{\rm i}, \Theta)\Theta{\rm d}\Theta \\ &\quad + 2\pi\int_{\Theta'}^{3\Theta'} \sigma_{\rm ap}(v_{\rm i}, \Theta)\Theta\sin^{-1}\frac{w}{l\Theta}{\rm d}\Theta \\ &\quad + 4w/l\int_{3\Theta'}^{\pi} \sigma_{\rm ap}(v_{\rm i}, \Theta){\rm d}\Theta, \end{aligned} \tag{31}$$

where $\Theta' = w/l$. However, it is not appropriate to give an absolute value for the correction of the total cross section. It is better to use the ratio $\Delta Q_{\rm eff}(v_{\rm i})/Q_{\rm eff}(v_{\rm i})$. Thus, the correction factor for the above case is given by

$$\frac{\Delta Q_{\rm eff}(v_{\rm i})}{Q_{\rm eff}(v_{\rm i})} = \frac{\int_0^{\pi} R(\Theta)\sigma_{\rm ap}(v_{\rm i}, \Theta)\sin\Theta{\rm d}\Theta}{\int_0^{\pi}\sigma_{\rm ap}(v_{\rm i}, \Theta)\sin\Theta{\rm d}\Theta}. \tag{32}$$

If the width of the beam is larger than that of the detector, a part of the beam does not contribute to I_0 but some atoms in that part are scattered into the detector. In this case, the correction factor at constant l is given by

$$\frac{\Delta Q_{\rm eff}(v_{\rm i})}{Q_{\rm eff}(v_{\rm i})} = \frac{\int_0^{b_{\rm p}}\int_0^{\pi} i(z)R(z, \Theta)\sigma_{\rm ap}(v_{\rm i}, \Theta)\sin\Theta{\rm d}\Theta{\rm d}z}{\int_0^{w}\int_0^{\pi} i(z)\sigma_{\rm ap}(v_{\rm i}, \Theta)\sin\Theta{\rm d}\Theta{\rm d}z}. \tag{33}$$

If the values of b_p/l and w/l are smaller than the critical angle Θ^* which corresponds to θ^*, the R-functions which contribute mostly to the correction value are independent of z. Thus, Eq. (33) is approximated by

$$\frac{\Delta Q_{\rm eff}(v_{\rm i})}{Q_{\rm eff}(v_{\rm i})} \simeq F \times \frac{\int_0^{\pi}\bar{R}(\Theta)\sigma_{\rm ap}(\Theta)\sin\Theta{\rm d}\Theta}{\int_0^{\pi}\sigma_{\rm ap}(\Theta)\sin\Theta{\rm d}\Theta}, \tag{34}$$

where

$$F = \frac{\int_0^{b_{\rm p}} i_0(z){\rm d}z}{\int_0^{w} i_0(z){\rm d}z}, \tag{35}$$

and

$$\bar{R}(\Theta) = \frac{\int_0^{b_{\rm p}} i_0(z)R(z, \Theta){\rm d}z}{\int_0^{b_{\rm p}} i_0(z){\rm d}z}. \tag{36}$$

The value of F is obtained from the geometrical relation between the beam profile and the detector width, and the value of the $\bar{R}$-function can be easily calculated by a computer.

The more complete correction formula for the angular resolution is

$$\frac{\Delta Q_{\rm eff}(v_{\rm i})}{Q_{\rm eff}(v_{\rm i})}=\frac{\int_{l_{\rm cd}-L}^{l_{\rm cd}}\int_{-b_{\rm p}}^{b_{\rm p}}\int_{0}^{\pi} i_0(z){\rm e}^{-nQ(l_{\rm cd}-l)}R(z,l,\Theta)\sigma_{\rm ap}(v_{\rm i},\Theta)\sin\Theta {\rm d}z{\rm d}l}{\int_{l_{\rm cd}-L}^{l_{\rm cd}}\int_{-{\rm Min}[b_{\rm p},w]}^{{\rm Min}[b_{\rm p},w]}\int_{0}^{\pi} i_0(z){\rm e}^{-nQ(l_{\rm cd}-l)}\sigma_{\rm ap}(v_{\rm i},\Theta)\sin\Theta {\rm d}\Theta{\rm d}z{\rm d}l}, \quad (37)$$

where L is the effective length of the scattering chamber. However, if $l_{\rm cd}$ is much greater than L, Eq. (33) can be used as a satisfactory correction for angular resolution.

4. Application

Equation (34) has been applied to the previous experimental data.[1] The $\bar{R}$-function expressed by Eq. (36) was calculated by a computer for $b_{\rm p}=0.049$ mm, $b_{\rm u}=0.02$ mm, $w=0.0175$ mm, and $l=85$ mm. The $\bar{R}$-function has an asymptote at $\Theta \gg 2w/l$ as shown in Fig. 4. In order to obtain the apparent differential cross sections, Eq. (20) was also calculated by a computer by means of the Monte Carlo method. In this calculation the van der Waals constants obtained in the previous paper were used.[1] In Fig. 5 the apparent differential cross sections multiplied by $2\pi \sin\Theta$ are shown for the several different beam velocities in K–Ar system. Shaded areas show the correction parts of the total cross sections given by

$$2\pi\int_0^{\pi}\bar{R}(\Theta)\sigma_{\rm ap}(\Theta)\sin\Theta{\rm d}\Theta \quad (38)$$

In Eq. (34), F is the ratio of the beam profile to that covered by the detector, and the denominator is equal to the effective total cross sections obtained by the experiment. Values of Eq. (34) were estimated for the various primary beam velocities and are shown in Fig. 6 together with the values calculated by Busch's formulas,[6] the latter being a little larger. It should be noted that our correction factors do not vary as $v_{\rm i}^{4/5}$ as is predicted by Busch, and for K–Ar system the values become larger in low velocity range. It shows that Busch's approximation can not be applied to a

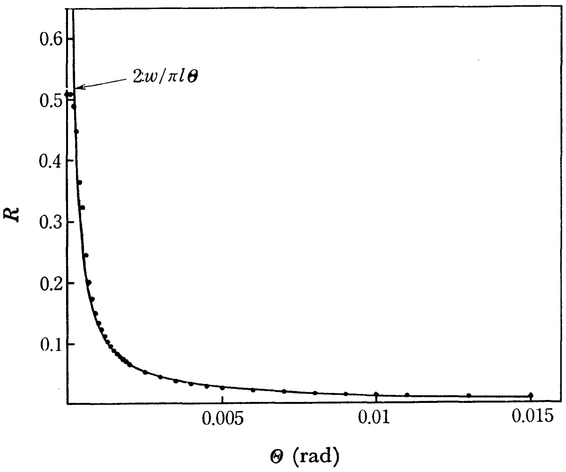

Fig. 4. Plot of $R(\Theta)$ calculated for the previous experimental parameters.

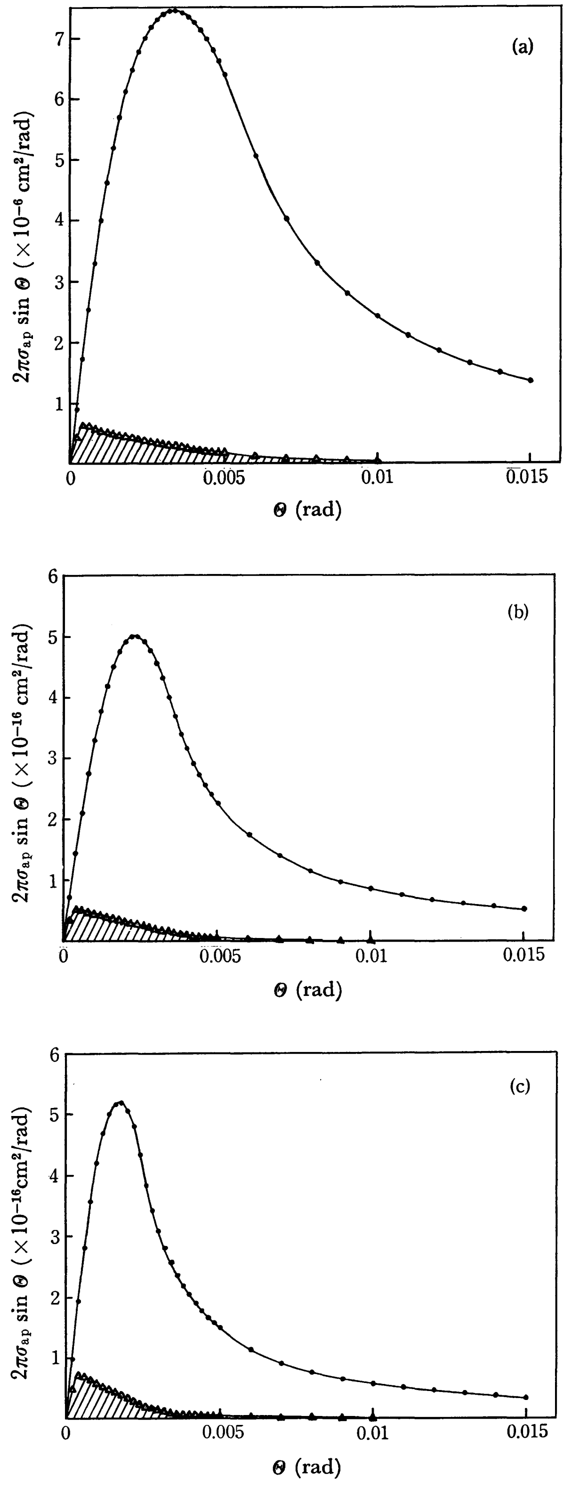

Fig. 5. Differential cross sections at small angles in the laboratory system.
K–Ar system. (a) $v_{\rm i}=400$ m/s, (b) $v_{\rm i}=720$ m/s, (c) $v_{\rm i}=1100$ m/s.
Shaded areas show the parts deflected into the detector.

6) Busch gave different formulas for the correction of the angular resolution in Ref. 2 and in *Z. Phys.*, **199**, 518 (1967). The values calculated by the formula in Ref. 2 are smaller than in the other paper.

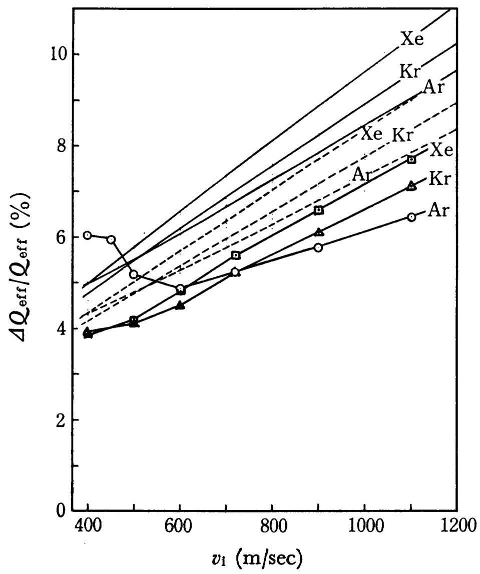

Fig. 6. Plots of $\Delta Q_{eff}(v_i)/Q_{eff}(v_i)$ for K–Ar, K–Kr, and K–Xe systems. Curves were obtained from Busch's formulas;

$$\frac{\Delta Q}{Q} = 0.0765\sqrt{Qk_i^2\gamma}\left(1+\frac{0.368}{x^2}\right) \text{ for the solid curve,}$$

$$\frac{\Delta Q}{Q} = 0.0665\sqrt{Qk_i^2\gamma}\left(1+\frac{0.376}{x^2}\right) \text{ for the dashed curve.}$$

case under usual experimental conditions in the thermal energy range.

In the above calculation to estimate correction ratio the van der Waals constants given in the previous paper were used. The correction applied there was not as good as here. However, the correction ratio varies only slightly with the change of constant value. For example, ten percent change of the value of C in K–Ar system results in five percent change of $\Delta Q_{eff}/Q_{eff}$ at $v_i=720$ m/sec. Therefore, the values of the absolute effective total cross section estimated by the present method were hardly affected by the applied values of C. Therefore, if we start with a reasonable value of C, the estimated C will be almost similar to the initial one.

To reestimate the previous experimental data, the effective total cross sections have been corrected for the angular resolution using the values in Fig. 6 at first. Following the procedure, the effective total cross sections have been corrected by the thermal motion of the target gases, and the absolute total cross sections Q_w were obtained. The van der Waals constants reestimated from these Q_w are

$$C_{K-Ar} = 231\times10^{-60}\ \text{erg}\cdot\text{cm}^6$$
$$C_{K-Kr} = 337\times10^{-60}\ \text{erg}\cdot\text{cm}^6$$
$$C_{K-Xe} = 515\times10^{-60}\ \text{erg}\cdot\text{cm}^6$$

These values are a little smaller than the previous values. However, the conclusions in the previous paper have not been affected by the present procedure.

The author would like to thank Professor Kumasaburo Kodera for his valuable advice. The FACOM 230-60 computer system of Kyoto University was used for the calculation.