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OBSERVATIONS OF RAINBOW SCATTERING IN CROSSED MOLECULAR BEAMS: K + COS AND K + CS_2

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Differential elastic scattering cross sections have been measured for the systems K + COS and CS_2 at different energies in the thermal energy range. The intermolecular potential well depths have been evaluated from the rainbow scattering. The evaluated values ε for the Lennard-Jones(12,6) potentials were 0.37 Kcal/mole for K + COS and 0.41 Kcal/mole for K + CS_2, respectively.

The rainbow effect due to the elastic scattering in crossed molecular beams gives information about an intermolecular potential. The effect was observed for certain systems by two groups in 1961.[1] Since then, the group of Brown University has observed the effect for many systems of alkali + halogen compounds.[2] However, in Ham and Kinsey's paper the effect has not been seen clearly for the systems of alkali + oxygen compounds (K + CO_2, SO_2). The lack of the distinct rainbow peak may be attributed to, (1) quenching due to the formation of long-lived collision complexes proposed by them, (2) quenching due to the non-spherical nature of their molecules, and/or (3) merely by the inadequate angular resolution. In the present paper COS and CS_2 were used for secondary beams and the rainbow effects have been observed.

Experimental

The apparatus consisted of five chambers (labelled A,B,---,E) as shown in Fig.1. A source for potassium beam was placed in the chamber labelled A, a velocity selector was set in the chamber B, and the chambers C and D were used to form a secondary beam. In the chamber E two beams were crossed at 90°, and

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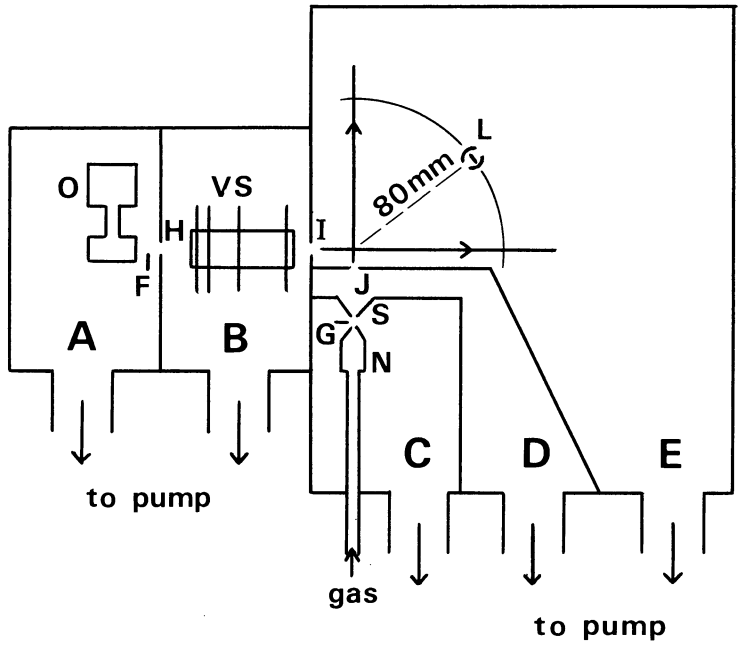

O, potassium oven
F,G, beam flags
H,I,J, collimating slits
VS, mechanical velocity selector
N, nozzle
S, conical skimmer
L, detector

Fig. 1, Schematic drawing of the crossed-beam apparatus.

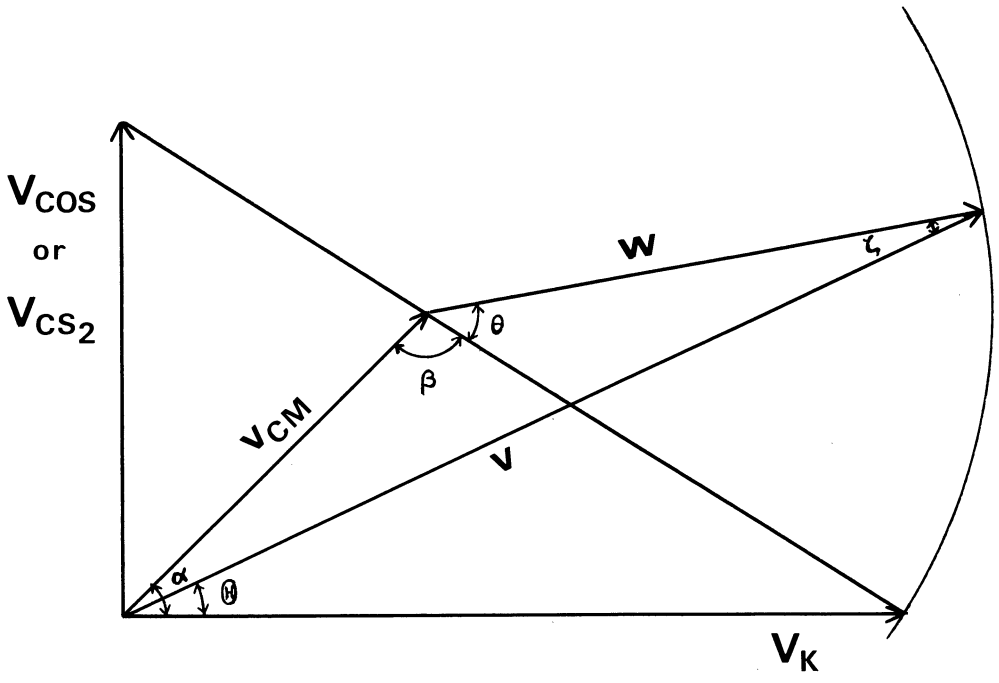

Fig. 2, Velocity diagram for elastic scattering in the plane of the two beams.

a part of the beam particles were scattered at the crossed region. A detector for potassium atoms could be rotated around the scattering center from -5° to 90° in the plane of the two beams. The chambers A, B, and D were separately pumped by 700 l/sec oil diffusion pumps with liquid-nitrogen traps, and the chambers C and E by 1800 l/sec oil diffusion pumps with water cooled baffles, respectively. In the chambers A and E there were large liquid-nitrogen cooled plates to reduce the background from the scattered beams. The background pressures in these chambers were kept in the range from 2×10^{-6} to 2×10^{-7} Torr during measurements.

The potassium atoms effused from a double-chamber type oven (slit width 0.16 mm) were velocity selected by a slotted disk type selector ($\Delta v/v = 4.7$ %, 120 mm long),[4] and then collimated into a beam of 0.5°FWHM (full width at half maximum) by an entrance slit I (width 0.5 mm) of the scattering chamber E. The secondary beam (COS, or CS_2) expanded from a 0.1 mm nozzle passed through a 0.45 mm conical skimmer and collimated with an entrance slit J (width 0.45 mm) into the scattering chamber E. The secondary beam had about 0.8°FWHM at the scattering zone. The most probable speed of the nozzle beam was estimated by

$$\frac{v_s}{v_p} = M_s \left(\frac{\gamma}{3} \frac{T_s}{T_o} \right)^{\frac{1}{2}} , \qquad (1)$$

where v_s is the most probable speed in a nozzle beam, v_p the most probable speed in an effusion beam, γ is the specific heat ratio, T_o and T_s are respectively the temperatures of the gas before and after the expansion, and M_s is the Mach number at the skimmer. The Mach number was estimated from the ratio of L to D, where L is the distance from nozzle to skimmer and D the diameter of nozzle opening. In this work the typical nozzle-skimmer distance was about 1 mm, and L/D was about 10. According to the calculation of Owen and Thornhill[5] the Mach number M_s under the condition of L/D = 10 should be about 9. There are two merits in using a nozzle beam, one of them is a high intensity and the other is a narrow velocity distribution in the beam. The pressures inside the nozzle were adjusted in the range of 50 to 200 Torr to keep the attenuation of the primary beam between 10 to 20 %.

The surface ionization detector for potassium atoms consisted of a 0.5 mm wide and 30 mm high Pt-W 8% ribbon. Typical primary beam signals were on the order of 10^{-9} A, and the scattered beam signals at large angles were on the order of 10^{-14} A. The scattered intensity at each angle was determined by on-off of the flag for the primary beam or for the secondary beam. The stepwidth for the angular setting was 0.5 .

Results and Discussion

A scattered beam signal $I(\Theta)$ at the laboratory (LAB) angle Θ can be related to a differential cross section $\sigma(\theta)$ at a center-of-mass (c.m.) angle θ. To show the relationship between the LAB angle Θ and the c.m. angle θ, a velocity diagram is shown in Fig.2, assuming an elastic scattering. The conversion from Θ to θ

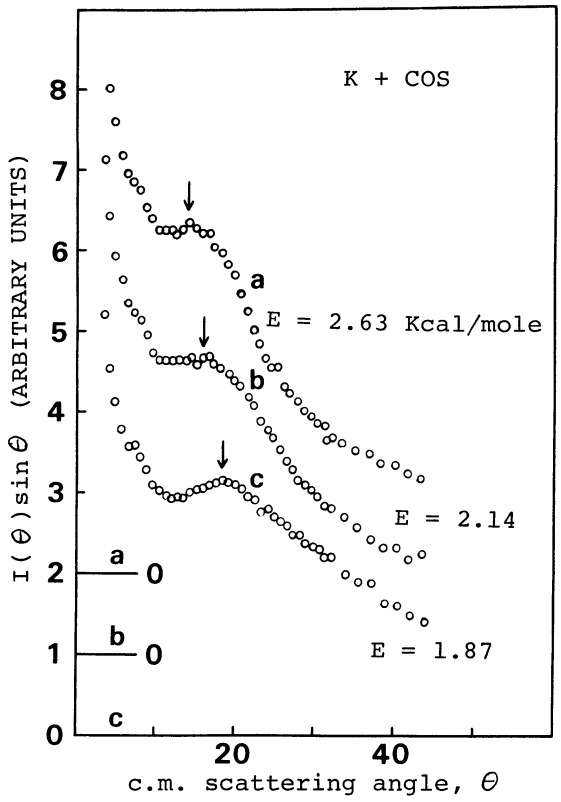

Fig.3, The differential elastic scattering cross section multiplied by $\sin\theta$ vs. the c.m. scattering angle θ for the system K + COS at three relative energies. E is the most probable c.m. energy. The rainbow maxima estimated with the assumed potential parameters are shown with arrows.

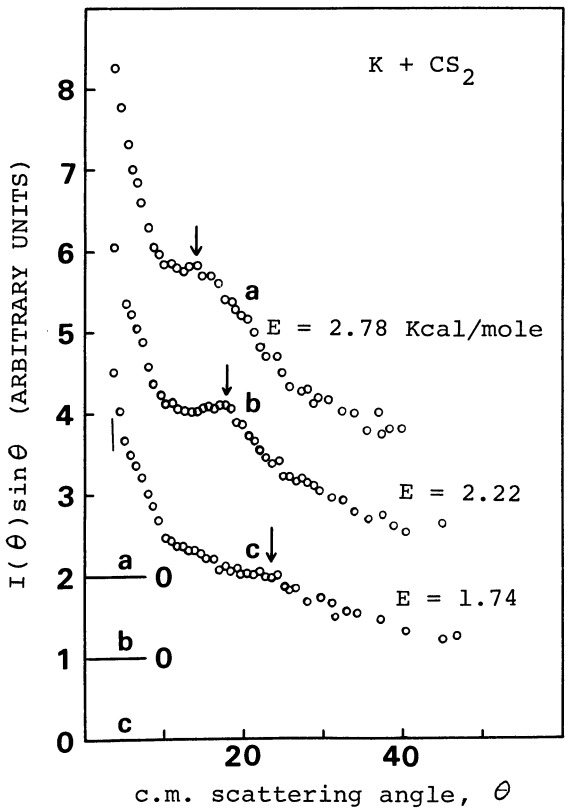

Fig.4, The differential elastic scattering cross section multiplied by $\sin\theta$ vs. the c.m. scattering angle θ for the system K + CS_2 at three relative energies. E is the most probable c.m. energy. The rainbow maxima estimated with the assumed potential parameters are shown with arrows.

is then given by

$$\frac{\sin(\alpha - \Theta)}{w} = \frac{\sin\{\pi - (\alpha - \Theta) - (\beta + \theta)\}}{v_{CM}} \quad , \qquad (2)$$

where w is the speed of the potassium atom in the c.m. system, v_{CM} the speed of the center-of-mass, α and β are the angles shown in Fig.2. The differential cross section $\sigma(\theta)$ will be proportional to $I(\Theta)$ and is expressed by

$$\sigma(\theta) \propto I(\Theta)\left(\frac{w}{v}\right)^2 |\cos\zeta| \quad , \qquad (3)$$

where v is the speed of potassium atom in the LAB system, ζ is the angle shown in Fig.2. In the above discussion, however, the velocity distribution of atoms in the beams and the volume of the scattering zone are ignored for simplicity.

The experimental results for the scattering of K by COS and CS_2 in the c.m. system are given in Figs. 3 and 4. The ordinates in the figures are proportional to $\sigma(\theta)\sin\theta$. The observed peak positions for the primary rainbow maximum depend on the relative kinetic energies E and shift to small angles in high energies. The effects of supernumerary rainbows expected from an Airy-approximation analysis[6] can be observed at small angles, but the positions of the maxima can not be decided unambiguously due to an overwhelming small-angle scattering. Thus, only angles of the primary rainbow maxima were used for the present analysis.

The rainbow angle θ_r with classical theory has been given for various spherically symmetrical potentials in the literatures,[7] and is a function of reduced kinetic energy $K = E/\varepsilon$. In the present analysis the values calculated for the Lennard-Jones (12,6) potential in Ref.7 (c) were used. The angle θ_{max} for the primary rainbow maximum may be related to the classical rainbow angle θ_r by the Airy-approximation[8]

$$\theta_{max} = \theta_r - 1.0188\left(\frac{q}{A^2}\right)^{\frac{1}{3}} \quad , \qquad (4)$$

where q is the second derivative of the classical deflection function at the minimum, and $A = kr_m$ is the reduced wave number. The parameter $k = \mu g/\hbar$ is the wave number, μ being the reduced mass, and g the relative velocity. The potential parameters ε and r_m are the well depth and the internuclear distance at the minimum in V(r), respectively. Assuming the values of these potential parameters, we can estimate the angle θ_{max} for a relative kinetic energy E from Eq.(4). Therefore, the best fit for θ_{max} at various relative kinetic energies should yield a set of the most probable parameters (ε, r_m). However, the positions of θ_{max} do not change appreciably with the value of r_m, yielding almost a constant value of ε for r_m between 4Å and 6Å. Therefore, assuming r_m = 5Å, the best values estimated for ε were

ε = 0.37 Kcal/mole for the system K + COS,

ε = 0.41 Kcal/mole for the system K + CS_2.

The spherically symmetrical potentials may not be appropriate for the linear molecules such as COS, and CS_2. Therefore, the parameters determined in the present work might be those for effectively spherical potentials averaged over

orientation of the molecules. The observed broadness of the rainbow peak may also be attributed to the anisotropy of the potential. For these systems quenching in the rainbow peaks may also be caused by the inelastic collisions resulting in rotational excitation and de-excitation of the molecules. In this paper, however, the quenching in the rainbow peaks will not be discussed further because of the absence of a satisfactory theory on this phenomena.

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REFERENCES

1) (a) Brown group: D.Beck, E.F.Greene, and J.Ross, Ⅱ ICPEAC,Abs. p.94 (1961); (b) Michigan group: F.A.Morse, R.B.Bernstein, and H.U.Hostettler, J.Chem.Phys., 36, 1947 (1962).
2) (a) D.Beck, J.Chem.Phys., 37, 2884 (1962); (b) D.Beck, E.F.Greene, and J.Ross, ibid., 37, 2895 (1962); (c) M.Ackerman, E.F.Greene, A.L.Moursund, and J.Ross, ibid., 41, 1183 (1964); (d) J.R.Airey, E.F.Greene, K.Kodera, G.P.Reck, and J.Ross, ibid., 46, 3287 (1967); (e) J.R.Airey, E.F.Greene, G.P.Reck, and J.Ross, ibid., 46, 3295 (1967); (f) E.F.Greene, E.F.Hoffman, and M.W.Lee, ibid., 50, 3450 (1969).
3) D.O.Ham and J.L.Kinsey, J.Chem.Phys., 53, 285 (1970).
4) K.Kodera, I.Kusunoki, and H.Matsumoto, Oyobutsuri (in Japanese), 41, 24 (1972).
5) P.L.Owen and C.K.Thornhill, Aeronautical Reseach Council (U.K.) R & M No. 2616 (1948); see also the review of supersonic nozzle beams by J.B.Anderson, R.P. Andres, and J.B.Fenn in J.Ross, ed., "Molecular Beams" (Advances in Chemical Physics Vol.10), Interscience Publishers, New York, 1966, p.286.
6) (a) E.A.Mason and L.Monchick, J.Chem.Phys., 41, 2221 (1964); (b) E.Hundhausen and H.Pauly, Z.Naturforsch., 19a, 810 (1964).
7) (a) E.A.Mason, J.Chem.Phys., 26, 667 (1957); (b) Ch.Schlier, Z.Physik, 173, 352 (1963); (c) G.E.Ioup and B.S.Thomas, J.Chem.Phys., 50, 5009 (1969).
8) K.W.Ford and J.A.Wheeler, Ann.Phys.,N.Y., 7, 259 (1959); see also Ref.6.

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