Rainbow Scattering in Collisions of Low Energy Argon Ions with Methane Molecules

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Peaks due to the rainbow scattering in elastic collisions of Ar^+ ions with ground state CH_4 molecules were observed in the differential cross section at laboratory energies from 20 to 80 eV superimposed on an oscillatory structure which is attributed to the accidental resonant electron transfer between collision partners. The rainbow peaks are clearly seen when the differential cross section is plotted in a reduced form. Indeed, each rainbow peak appears at the reduced scattering angle of about 290 eV-degrees. Classical calculations are fitted to the experimental cross sections with the use of the 12-6-4 potential. This potential contains an adjustable force parameter γ ranging from 1 to 0 according to how the charge-induced dipole interaction has a dominant role in the collision. The best fit is obtained when the potential depth is 2.7 eV and the inter-atomic distance at the potential well minimum is 2.4 Å for $\gamma = 0.4$.

1. Introduction

In the previous paper¹⁾ we reported measurements of differential cross sections in collisions of low energy Ar^+ ions with ground state CH_4 molecules, in which we observed a relatively smooth oscillatory structure superimposed on a monotonically decreasing function due to the elastic collision. These oscillations were there treated qualitatively in terms of the Jahn-Teller effect interpreting as an interference between symmetrical and antisymmetrical potentials of pseudo-molecular (Ar-CH_4)⁺

ions.

In addition to these oscillations apparently abrupt change of the envelope of the oscillation was observed at a certain scattering angle. When experimental cross sections are plotted in the reduced differential cross sections against the reduced scattering angles, these irregularities in the differential cross sections show prominent peaks at almost the same reduced scattering angles. Therefore, we attribute these peaks to the rainbow scattering.²⁾ The rainbow scattering is also due to an interference between different partial

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waves elastically scattered from the interaction potential concerned. The measurement of the rainbow scattering is important in that the potential parameters can be obtained from the angular position and the shape of the rainbow peak, and hence many works of this kind have been carried out up to the present and are summarized in various review papers.³⁻⁶⁾

In this paper we will present a simple classical fitting method to derive the potential parameters from the rainbow peaks. This method saves many numerical labours as compared with those of a semi-classical or a quantal treatment, and it seems to be useful especially for an experiment of relatively low angular resolution where only a single rainbow undulation without supernumerary rainbows or a rainbow peak with other interference oscillation is obtained as is the present case. The accuracy of this method will be discussed.

2. Experimental Results

Measurements of the rainbow scattering made by using a crossed-beam apparatus are presented in this section. Experimental apparatus used in this study is the same as that described in the previous papers.^{7,8)}

The differential cross section obtained in the experiment exhibits a single rainbow undulation superimposed on oscillations due to the accidental resonant electron transfer reaction as described in the previous paper.¹⁾ It is in general difficult to separate the rainbow peak alone from these oscillations. However, in order to emphasize the rainbow peak in the differential cross section in a reduced form, i. e., in terms

of the reduced differential cross section, $\rho(\theta) = \theta \cdot \sin \theta \cdot \sigma(\theta)$, and the reduced scattering angle, $\tau = E \cdot \theta$. Here $\sigma(\theta)$, θ , and E are the differential cross section, the scattering angle and the collision energy in the center-of-mass system respectively. By this procedure the strong angular dependence of the differential cross section can be eliminated and the rainbow peaks are presented at approximately the same reduced scattering angle independent of the collision energy.

In Fig. 1 experimental differential cross sections are plotted in the reduced form $\rho(\theta)$ against the reduced scattering angle τ for two different incident energies. As is apparent in the figure, both reduced cross sections show prominent rainbow peaks at the reduced scattering angle of about $\tau = 290$ eV-degrees. Oscillatory structures on both wings of the rainbow peak are, as mentioned above, attributed to the interferences resulted from the accidental resonant electron transfer between Ar^+ ions and CH_4 molecules during the collision. The potential parameters can be decided from angular positions and dark-side shapes of the rainbow peaks. The classical fitting procedure will be presented in the following sections.

3. Expansion of the Classical Deflection Function

We have derived previously a generalized formula for the classical deflection function in a multiple series of inverse square of the impact parameter.⁹⁾ This series holds for any combinations of attractive and repulsive potentials of the form

$$\frac{V(r)}{E} = -\sum_j \frac{c_j}{r^{2m_j}} \quad (1)$$

where $V(r)$ denotes the interaction potential at the interatomic distance r , E is the relative kinetic energy, m_j is an integer greater than unity, and c_j is a coefficient which is positive for an attractive potential and negative for a repulsive potential. For this potential the classical deflection function χ can be expanded in the inverse square power of the impact parameter as given by

$$\chi = -\sum_{n=1}^{\infty} \sum_i \frac{(c_i b^{-2m_i})^{n_1}}{n_1!} \frac{(c_2 b^{-2m_2})^{n_2}}{n_2!} \frac{(c_3 b^{-2m_3})^{n_3}}{n_3!} \dots \frac{\Gamma(1/2) \Gamma(\sum_i n_i m_i + 1/2)}{\Gamma(\sum_i n_i m_i - n + 1)} \quad (2)$$

where b is the impact parameter and Γ is the Gamma function. The detail of the derivation of this formula and criterion on the convergence of this series will be presented elsewhere. This series expansion is a generalization of the formula derived first by Kihara¹⁰ and later by Smith¹¹ for the monomial potential of the form $c r^{-n}$.

As a model potential, we employ the widely used 12-6-4 potential of the form

$$V(r) = \frac{\epsilon}{2} [(1+\gamma) (r_m/r)^{12} - 4\gamma (r_m/r)^6 - 3(1-\gamma) (r_m/r)^4], \quad (3)$$

where ϵ is the depth of the potential well, r_m is the interatomic distance at which the potential becomes minimum, and γ is an adjustable force parameter ranging from 1 (neutral-neutral scattering) to 0 (extreme case of ion-neutral scattering). In usual ion-neutral scattering the value of γ falls between 1 and 0. For this potential

the deflection function (2) can be written by

$$\chi = -\frac{1}{2K} \sum_{n=1}^{\infty} \sum_i \frac{\{(1+\gamma)\beta^{-12}\}^{n_1}}{n_1!} \cdot \frac{\{-4\gamma\beta^{-6}\}^{n_2}}{n_2!} \cdot \frac{\{-3(1-\gamma)\beta^{-4}\}^{n_3}}{n_3!} \cdot \frac{\Gamma(1/2) \Gamma(\sum_i n_i m_i + 1/2)}{\Gamma(\sum_i n_i m_i - n + 1)}, \quad (4)$$

where K is the reduced kinetic energy (E/ϵ), β is the reduced impact parameter (b/r_m), and m_i is 6, 3 or 2 corresponding to the suffices $i = 1, 2$ or 3 respectively.

The convergence of this series for the potential (3) is fairly rapid so far as the reduced kinetic energy K is not too large,¹² so the first term in the expansion of Eq. 4 is adequate in actual calculations. It is shown that the expression of the classical deflection function derived previously by means of the Mellin transformation¹³ corresponds to the first term of this series.

4. Fitting to the Experimental Cross Section

Using the classical deflection function (4) in the previous section, the differential cross section $\sigma(\theta, K)$ can be calculated by the equation

$$\sigma(\theta, K) = r_m^2 \sum_{i=1}^3 \frac{\beta_i}{\sin \theta |d\chi/d\beta_i|}, \quad (5)$$

where the scattering angle is given by $\theta = |\chi|$, and the summation is made over three possible branches of the deflection function which contribute to the same scattering angle θ .

In order to compare the numerical calculations with experimentally obtained differential cross sections, the differential cross section (5) must be averaged over the angular spread due to the angular resolution of the apparatus and the energy spread in the primary ion beam. A gaussian distribution function was assumed for the energy spread of the primary ion beam. By this procedure the singularity in Eq. 5 was smeared out to give a smooth rainbow undulation. Most calculations have been performed taking account of only the first term of the deflection function given by Eq. 4. Validities of this approximation have been examined by fitting the results to the experimental scattering data of $\text{Ar}^+ + \text{Ar}$ and $\text{Xe}^+ + \text{Xe}$ measured by Lorents, Olson and Conklin.¹³⁾ Apart from the oscillating patterns due to the resonant electron transfer interferences which are not responsible for the rainbow scattering, the calculated curves are fairly in good agreement with their data especially in the neighbourhood of the rainbow peaks. Results are seen elsewhere.^{9,14)}

5. Results and Discussion

Potential parameters obtained by fitting the calculations to experimental differential cross sections will be presented in this section. In the calculations we have assumed the angular resolution of the apparatus $\Delta\theta_{\text{lab}}$ to be 0.75° and the relative energy spread in the primary beam $\Delta K/K$ to be 0.05, respectively.

The best fit is obtained when the potential well depth ϵ is 2.7 eV and the interatomic distance at the potential minimum r_m is 2.4 Å for the adjustable force para-

meter $\gamma = 0.4$. Resulted curves are shown in Fig. 1 with solid lines. As a trial value

Fig. 1. Reduced differential cross sections, $\rho(\theta) = \theta \sin \theta \sigma(\theta)$, are plotted against reduced scattering angle, $\tau = E \theta$, for collisions of Ar^+ with CH_4 . Classical calculations (solid line) are fitted to experiments (closed circle). The best fit is obtained for $\epsilon = 2.7$ eV and $r_m = 2.4$ Å, assuming the 12-6-4 potential.

of the potential depth in interactive calculations, we have referred an approximate formula which gives the relation between the rainbow angle θ_R and the potential depth ϵ as given by¹⁵⁾

$$-\theta_R(E/\epsilon) \simeq 0.29\gamma + 1.75, \quad (6)$$

where E denotes the kinetic energy of the primary beam in the center-of-mass frame, and γ is the force parameter in Eq. 3. The trial potential depth estimated from Eq. 6 is, for example, 2.6 eV for the incident beam energy of 33.1 eV (9.47 eV in center-

of-mass energy) for $\gamma=0.4$. Starting from this value iteration has been performed to get the best fitted value of 2.7 eV.

It can be shown from the rainbow scattering data of $\text{He}^+ + \text{CH}_4$ previously measured¹⁹⁾ that the potential depth of 2.7 eV occurring at about 290 eV-deg is reasonable. If it is assumed that the shape of the $\text{Ar}^+ - \text{CH}_4$ potential minimum region is similar to that of $\text{He}^+ - \text{CH}_4$, then the value of the $\text{Ar}^+ - \text{CH}_4$ well depth ϵ_{Ar} is approximately given by the relation¹⁹⁾

$$\epsilon_{\text{Ar}} \simeq \frac{\tau_{\text{Ar}}}{\tau_{\text{He}}} \epsilon_{\text{He}}, \quad (7)$$

where τ_{Ar} and τ_{He} represent the reduced scattering angle ($\tau = E \cdot \theta_R$) for $\text{Ar}^+ - \text{CH}_4$ and $\text{He}^+ - \text{CH}_4$ collisions, respectively, and ϵ_{He} is the value of the $\text{He}^+ - \text{CH}_4$ potential minimum. The relation (7) can be deduced directly from the formula (6). Taking the rainbow scattering data of $\text{He}^+ + \text{CH}_4$ from the previous paper¹⁹⁾ as $\tau_{\text{He}} = 158$ eV-deg and $\epsilon_{\text{He}} = 1.5$ eV for $\gamma = 0.4$, we have the potential depth ϵ_{Ar} to be 2.75 eV. This value is in extremely good agreement with that obtained by fitting procedure.

The value of r_m can be obtained from the dark side shape of the rainbow undulation. However, the determined value is very sensitive to the curve shape and is not necessarily reliable as compared with that of the potential depth. Therefore, it only offers a measure of the trial value of r_m for iterative fitting calculations. We have referred to the semiclassical relation for the value of r_m as given by¹⁾

$$r_m = \frac{\sqrt{\eta}}{\kappa} (1.0188/\Delta\theta_R)^{3/2}, \quad (8)$$

where $\kappa = [2\mu\epsilon(K+1)/\hbar^2]^{1/2}$ is the wave number of the incoming wave, μ is the reduced mass, $\Delta\theta_R$ is the angular distance between the rainbow maximum and the true rainbow angle, and η is one-half of the second derivative of the classical deflection function with respect to the reduced impact parameter as given by (1/2) $[d^2\chi/d\beta^2]_{\beta=\beta_R}$. Though there is no extensive physical meaning that the semiclassical relation (8) stands for the present classical treatment, we assume that the true rainbow angle is located at the angular position where the cross section decreases by 44 % down from the the rainbow maximum as usually done in the semiclassical treatment. When the rainbow undulation is superim-

Fig. 2. The 12-6-4 potential for the $\text{Ar}^+ + \text{CH}_4$ system. The best fitted potential (solid line; $\epsilon = 2.7$ eV, $r_m = 2.4$ Å) is compared with that from the rainbow peak alone (dotted line: $\epsilon = 2.6$ eV, $r_m = 2.5$ Å).

posed on the oscillations which are attributed to other mechanisms, as the present case, we have to extrapolate the cross section with an appropriate function to estimate the true rainbow position. The choice of $\Delta\theta_R$ is, therefore, quite subjective, but this procedure is of necessity because we are not aware of any classical treatments to estimate the value of $\Delta\theta_R$. However, it will be shown below that the trial r_m -value derived by this procedure leads to a fairly good measure of the iterative fitting calculations.

From the definition of η given above, we can approximately relate the value of η to the potential depth ϵ by the relation¹²⁾

$$\eta(E/\epsilon) \simeq 56.7\gamma + 72.0, \quad (9)$$

where γ is again the adjustable force parameter of the 12-6-4 potential.

With the aid of Eqs. 8 and 9 and assuming the potential depth to be 2.60 eV and $\Delta\theta_R$ to be 2.3° from the experimental cross section for the incident beam energy of 33.1 eV, we have the trial value of r_m to be 2.5 Å for $\gamma=0.4$. Starting from these trial potential parameters, we have the best fitted potential parameters as $\epsilon = 2.7$ eV and $r_m = 2.4$ Å for $\gamma = 0.4$, respectively. It is generally considered that potential parameters obtained from the rainbow peak alone are not always reliable. However, both values obtained from the rainbow peak show fairly excellent agreement with those estimated by the fitting procedure. Potential curves for these two cases are shown in Fig. 2.

The present classical fitting method is lacking in accuracy as compared with the elaborate quantal treatment. However,

this method is simple and saves much numerical labour.

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References

- 1) T. Arikawa, *Mass Spectrosc.*, **31**, 45(1983).
- 2) E. A. Mason, *J. Chem. Phys.*, **26**, 667 (1957).
- 3) K. W. Ford and J. A. Wheeler *Ann. Phys. (N.Y.)*, **7**, 259, 287 (1959).
- 4) H. Pauly and J. P. Toennies, in "Advances in atomic and Molecular Physics," Vol. 1, Ed., D. R. Bates and I. Estermann, Academic Press, New York, p. 195 (1965).
- 5) M. A. D. Fluendy and K. P. Lwley, in "Chemical Applications of Molecular Beam Scattering," Chapman and Hall, London (1973).
- 6) T. Arikawa, *Mass Spectrosc.*, **25**, 117 (1977).
- 7) T. Arikawa, *Mass Spectrosc.*, **22**, 171 (1973).
- 8) T. Arikawa, *Mass Spectrosc.*, **22**, 173 (1974).
- 9) T. Arikawa and G. Iwata, *Mass Spectrosc.*, **22**, 225 (1974).
- 10) T. Kihara, *Proc. Phys. Math. Soc. Japan*, **25**, 73 (1943).
- 11) H. M. Smith, *Phys. Fluids*, **3**, 721 (1960).
- 12) T. Arikawa, T. Mochizuki, and G. Iwata, *Mass Spectrosc.*, **20**, 167 (1972).
- 13) D. C. Lorents, R. E. Olson, and M. Conklin, *Chem. Phys. Letters*, **20**, 589 (1973).
- 14) T. Arikawa and H. Higaki, *Mass Spectrosc.*, **24**, 225 (1976).
- 15) T. Arikawa and T. Mochizuki, *Mass Spectrosc.*, **20**, 249 (1972).
- 16) W. Aberth and D. C. Lorents, *Phys. Rev.*, **144**, 143 (1966).

Keywords

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