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THE RELATION BETWEEN MOMENTUM TRANSFER AND CAPTURE AND TOTAL SCATTERING CROSS SECTIONS FOR ION-DIPOLE COLLISIONS

by John V. Dugan, Jr.
Lewis Research Center
Cleveland, Ohio

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by John V. Dugan, Jr.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

ABSTRACT

Numerical values of momentum transfer cross sections σ_m for ion-dipole collisions are compared with the corresponding capture cross sections σ_c as a function of ion velocity and rotational temperature. For values of dipole moment μ from 1 to 4 Debyes the (σ_m/σ_c) ratio is in the range 1.2 to 2.0 (roughly). This is in contrast to the simple relation for Langevin collisions where $(\sigma_m/\sigma_c) \cong 1.10$ independent of polarizability of the target atom. At low temperatures, the momentum transfer cross sections can be as large as 2000 $Å^2$, but they are only about 15 to 30 percent of the total scattering cross sections σ_s.

INTRODUCTION

Total scattering cross sections for ion-dipole collisions have been calculated from a scattering ratio (refs. 1 and 2) just as capture cross sections for these encounters were calculated from a capture ratio (refs. 3-5). The total scattering cross section, σ_s, is

$$\sigma_s \equiv \pi \int_0^\infty C_s(b^2)d(b^2) \tag{1}$$

where C_s is the fraction of trajectories for which scattering in the center-of-mass system is greater than a minimum angle θ_o for a fixed impact parameter b. Generally one hundred trajectories were studied per point and results plotted as histograms of fractional scattering intensity $I_s(\theta)$ versus the scattering angle θ (in increments of 0.2 radians). This intensity $I_s(\theta)$ is already integrated over the incremental solid angle $\sin\theta\, d\theta\, d\Phi$ so that

$$\sum_{\theta_o}^{\pi} I_s(\theta)/I_o = C_s(b)$$

where I_o is the total number of trajectories studied at fixed b, i.e., the incident intensity. Results of $I_s(\theta)$ distributions are somewhat rough but indicate that there is considerable small angle scattering at large impact parameters, i.e., $25 \leq b \leq 50$ Å, so that total scattering cross sections σ_s range from 1000 to 8000 Å^2 (ref. 2).

DETAILS OF THE CALCULATION

The momentum transfer cross section which is of interest for the diffusion of ions through polar gases is effectively the total scattering cross section weighted for large angle scattering, i.e.,

$$\sigma_m \equiv C_o \frac{\pi}{I_o} \int_0^{\infty} d(b^2) \int_{\theta_o}^{\pi} I_s(\theta)(1 - \cos\theta)\, d\theta \qquad (2a)$$

where C_o is a normalization constant. Thus we can simply calculate this momentum transfer cross section from a modified scattering ratio C_s' via

$$\sigma_m \equiv \pi \int_0^{\infty} C_s'(b^2)\, d(b^2) \qquad (2b)$$

where the approximate scattering ratio is

$$C_s(b) \cong C_1 \sum_{\theta_0}^{\pi} I_s(\theta)\,(1 - \cos\theta) \tag{3}$$

C_1, the normalization constant, is the reciprocal of the incident intensity. The summation in Eq. (3) is done for equal 0.2 radian increments with $(1 - \cos\theta)$ in each case evaluated at the midpoint of the interval.

Total scattering cross sections calculated for symmetric top polar targets were larger than for linear molecules of identical dipole moment (refs. 1 and 2). This effect was expected on the basis of the Stark Effect (ref. 2). In the case of the momentum transfer cross section, however, the $(1 - \cos\theta)$ factor minimizes any significant differences in the amplitude of small angle scattering which is dominant at large impact parameters. Thus, momentum transfer cross sections for ions in polar gases are not expected to be very sensitive to target geometry.

Numerical calculations were done for ion velocities of 5×10^4 and 10^5 cm sec^{-1} and for target rotational temperatures of 77 and 300 K. Most of the data consists of 100 trajectory sets for fixed impact parameter b. The exception to this were 200 trajectory collision sets which were done for constant b to obtain a relatively smooth $I_s(\theta)$ for $T_R = 77$ K, $v = 5\times10^4$ cm sec^{-1}. Generally, the scattering distributions are somewhat rough. At first it might appear that $I_s(\theta)$ could be assumed independent of scattering angle at smaller impact parameters (<20 Å). However, scattering in multiple reflection encounters is not always isotropic in the center-of-mass system at the smaller impact parameters, and the single reflection captures result in mainly small-angle scattering, i.e., $\theta < 0.4$ radians (ref. 2).

RESULTS AND DISCUSSION

Results of scattering intensity $I_s(\theta)$ for symmetric top CH_3CN targets are shown versus scattering angle θ for $T_R = 77$ K at three different impact parameters in Figs. 1(a) to 1(c). Two hundred trajectories were solved for b = 10 Å, 15 Å, and 20 Å. As was mentioned, since nearly half the collisions are multiple reflections (corresponding to ion-molecule complex formation) at 10 and 15 Å it is expected that the $I_s(\theta)$ might be nearly isotropic. However, this is not the case at the lower impact parameter where $I_s(\theta)$ resembles a monotonically decreasing distribution mainly because of $I_s(\theta)$ for single reflection capture collisions (refs. 1 and 2). The results for b = 15 Å are much more nearly isotropic. In all cases the collisions with greater than 15 captures were assumed to have an isotropic distribution in θ.

The variation in $I_s(\theta)$ results suggests that scattering in ion-dipole captures is considerably different than the Langevin case where all scattering is isotropic for b values less than the critical impact parameter (ref. 6). A more systematic study of the variation of $I_s(\theta)$ with various collision parameters was not undertaken because the computer time necessary was prohibitive. However, comparison of the aforementioned results (for a dipole moment of 3.92 Debyes) with $I_s(\theta)$ for HC1 (μ = 1.08 Debyes) (to be discussed later) suggest a strong dependence of the form of the scattering intensity on dipole moment. Thus, the relation between σ_m and σ_c is not simple as in the Langevin case but rather a function of relative energy and molecular constants, particularly dipole moment.

Representative variations of C_s with b^2 for linear "CH_3CN" molecules (dipole moment and polarizability of CH_3CN) selected from heat baths at T_R = 77 and 300 K is shown in Fig. 2(a) for $v = 5\times10^4$ cm sec^{-1} (ref. 2). The open triangles are for an additional 100 cases and are an indication of the C'_s dependence on random number sets. Comparison between results for 100 case and 200 case trajectory sets at the same impact parameter suggest that C'_s can be estimated within 15 percent using only 100 trajectories at each impact parameter. The corresponding $C'_s(b^2)$ plots are shown in Figs. 2(b) and 2(c). Since there is considerable scattering intensity at small $\theta(\theta_o \leq \theta \leq 0.2$ rad) C'_s is considerably less than C_s at b = 25 Å. Also C'_s is not a simple monotonically decreasing function of b^2 as are C_s and capture ratio C_R. The capture cross section σ_c is simply defined in terms of the capture ratio

$$\sigma_c \equiv \pi \int_0^\infty C_R(b^2)d(b^2)$$

At smaller b values, as mentioned, the rough $I_s(\theta)$ cannot be approximated by a uniform scattering intensity so that C_s' is never as large as C_s. The momentum transfer cross section for $T_R = 77$ K is π times the integral under the curve in Fig. 2(b), i.e., $\cong 2100$ Å^2. The momentum transfer cross section is considerably less for the higher rotational temperature, $T_R = 300$ K, $\sigma_m \cong 1100$ Å^2 suggesting a rough dependence $\sigma_m \sim (T_R)^{-0.5}$ based on comparison for these two temperatures.

The variation of momentum transfer σ_m and capture cross sections σ_c with ion velocity is shown for $T_R = 77$ K in Fig. 3. These σ_m dependences on relative energy, $\epsilon^{-0.78}$, and rotational temperature, $T_R^{-0.45}$ are steeper than the $\epsilon^{-0.5}$ and $(kT_R)^{-0.43}$ dependences for σ_s, the total scattering cross section (refs. 1 and 2). The corresponding dependences for σ_c are $\cong \epsilon^{-0.76}$ and $kT_R^{-0.33}$ for CH_3CN.

Finally, the variation of momentum transfer cross section with dipole moment value is shown in Fig. 4 where C_s' results for CH_3CN (μ = 3.92 D. U.) are compared with results for HCl (μ = 1.08 D. U.) at $v = 5\times10^4$ cm sec^{-1}, $T_R = 77$ K. The σ_m value for HCl $\cong 485$ Å^2 is almost twice the corresponding capture cross section. The results indicate that σ_m values are nearly proportional to dipole moment just as in the case of the capture σ_c and total scattering cross sections σ_s.

Comparison of σ_m values with σ_c values is done for rotational temperatures T_R of 77 and 300 K at a velocity of $v = 5\times10^4$ cm sec^{-1} in Table I. All of the differences in cross sections are outside the numerical uncertainty due to different random number sets so the quantity σ_m/σ_c is meaningful.

CONCLUDING REMARKS

Momentum transfer cross sections, σ_m, for ion-dipole collisions are much larger than Langevin cross sections σ_L for non-polar molecules of moderate polarizability at rotational temperatures T_R of 300 K and 77 K. Also the σ_m values are generally about 1.2 to 2.0 times the corresponding capture cross section whereas the Langevin σ_m/σ_c is always 1.105. The σ_m values for ion-dipole systems are only a small fraction of total scattering cross sections σ_s. Thus the momentum transfer cross section is generally larger than the capture cross section but only 20 to 30 percent of the total scattering cross section. Diffusion coefficients for ions in polar gases should be smaller than for non-polar molecules. A more systematic study of the variation of σ_m with all collision parameters is desirable. It is also desirable to use larger random number sets in order to obtain smoother distributions in scattering intensity.

REFERENCES

1. J. V. Dugan, Jr. and J. L. Magee, Paper presented at 24th Annual Gaseous Electronics Conference, Gainesville, Florida, October 1971.

2. J. V. Dugan, Jr. and J. L. Magge, Submitted to J. Chem. Phys., (1972).

3. J. V. Dugan, Jr. and J. L. Magee, J. Chem. Phys., 47, 3103, (1967).

4. J. V. Dugan, Jr., J. H. Rice and J. L. Magee, Chem. Phys. Letters, 3, 323 (1969).

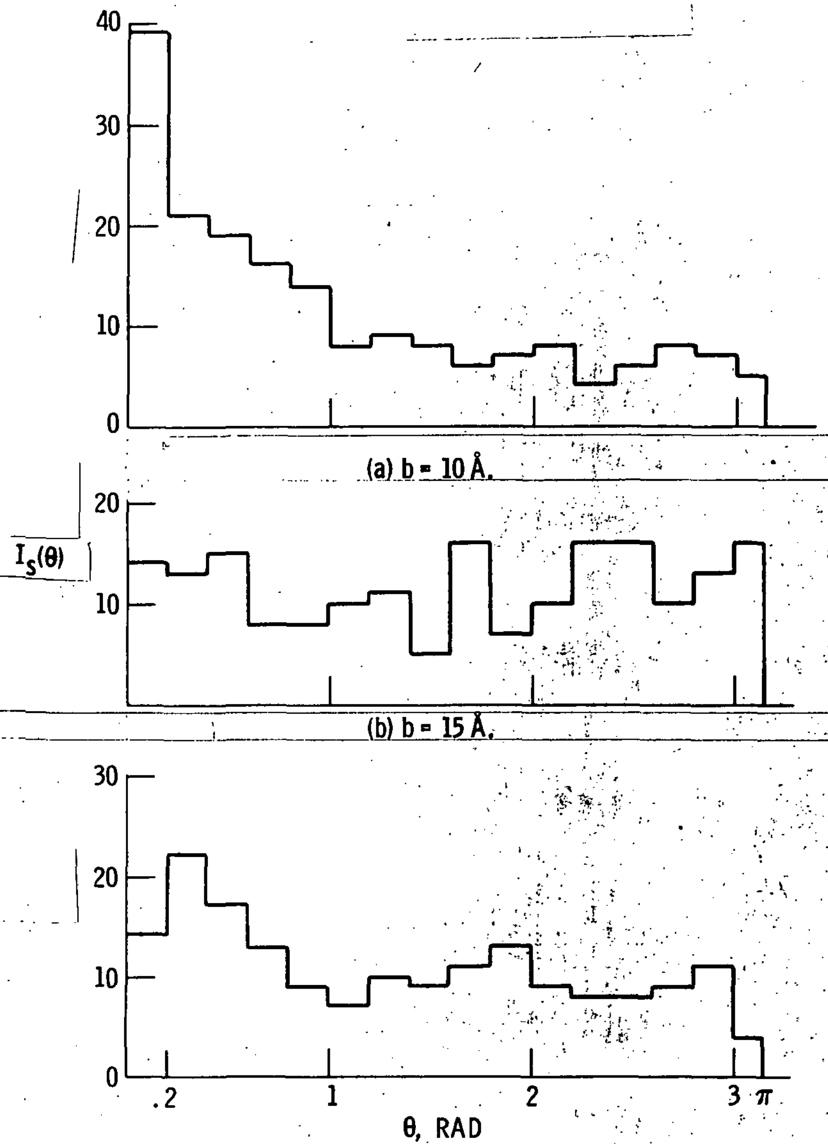
5. J. V. Dugan, Jr. and R. B. Canright, Jr., J. Chem. Phys., 56, 3623 (1972).

6. E. W. McDaniel, Collision Phenomena in Ionized Gases, (John Wiley and Sons, Inc., New York, 1964), Ch. 9, pp. 427-487.

CH_3CN, $v = 5\times10^4$ CM-SEC^{-1}

T_R, K	σ_m, Å^2	σ_c, Å^2
77	2000-2100	1310
300	1000-1100	750

Table I.

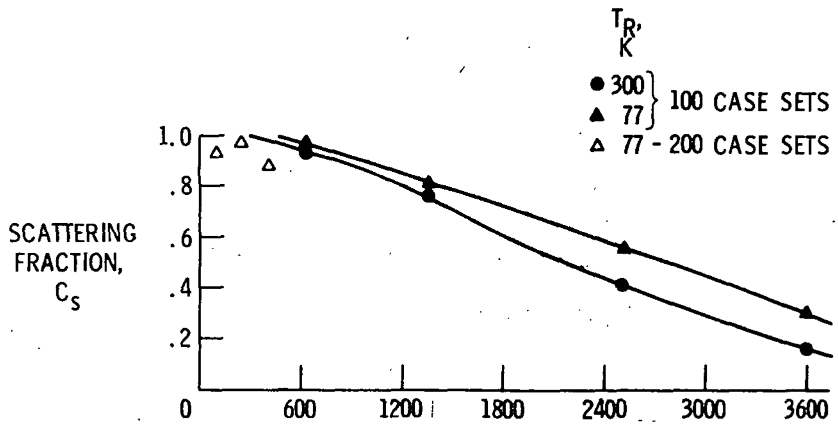


(a) b = 10 Å.

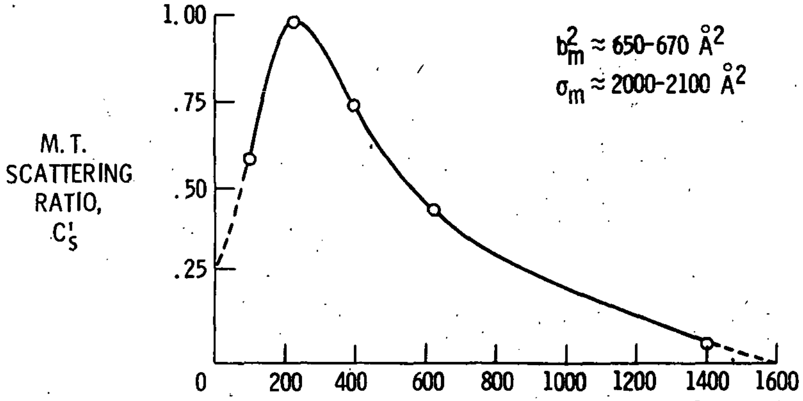
(b) b = 15 Å.

(c) b = 20 Å.

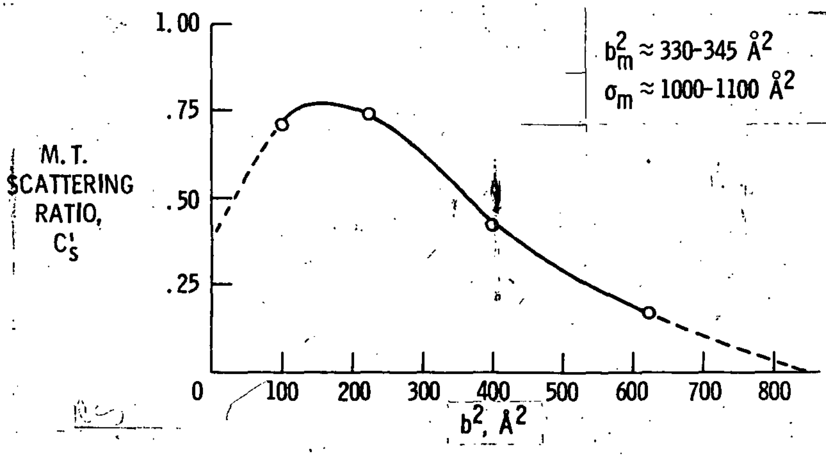
Figure 1. - Variations of scattering intensity with center-of-mass scattering angle for ion collisions with CH_3CN targets chosen from a bath at rotational temperature of T_R = 77 K for impact parameters of 10, 15, and 20 Å.



(a) VARIATION OF TOTAL SCATTERING CROSS SECTION WITH SQUARE OF IMPACT PARAMETER FOR ION COLLISIONS AT VELOCITY OF 5×10^4 CM SEC^{-1} WITH CH_3CN SYMMETRIC TOP TARGETS.



(b) VARIATION OF MOMENTUM TRANSFER SCATTERING RATIO WITH SQUARE OF IMPACT PARAMETER FOR ION COLLISIONS AT VELOCITY OF 5×10^4 CM SEC^{-1} WITH CH_3CN TARGETS CHOSEN FROM A BATH AT $T_R = 77$ K.



(c) VARIATION OF MOMENTUM TRANSFER SCATTERING RATIO WITH SQUARE OF IMPACT PARAMETER FOR ION COLLISIONS AT VELOCITY OF 5×10^4 CM SEC^{-1} WITH CH_3CN TARGETS CHOSEN FROM A BATH AT $T_R = 300$ K. (ALL 100 CASE SETS.)

Figure 2.

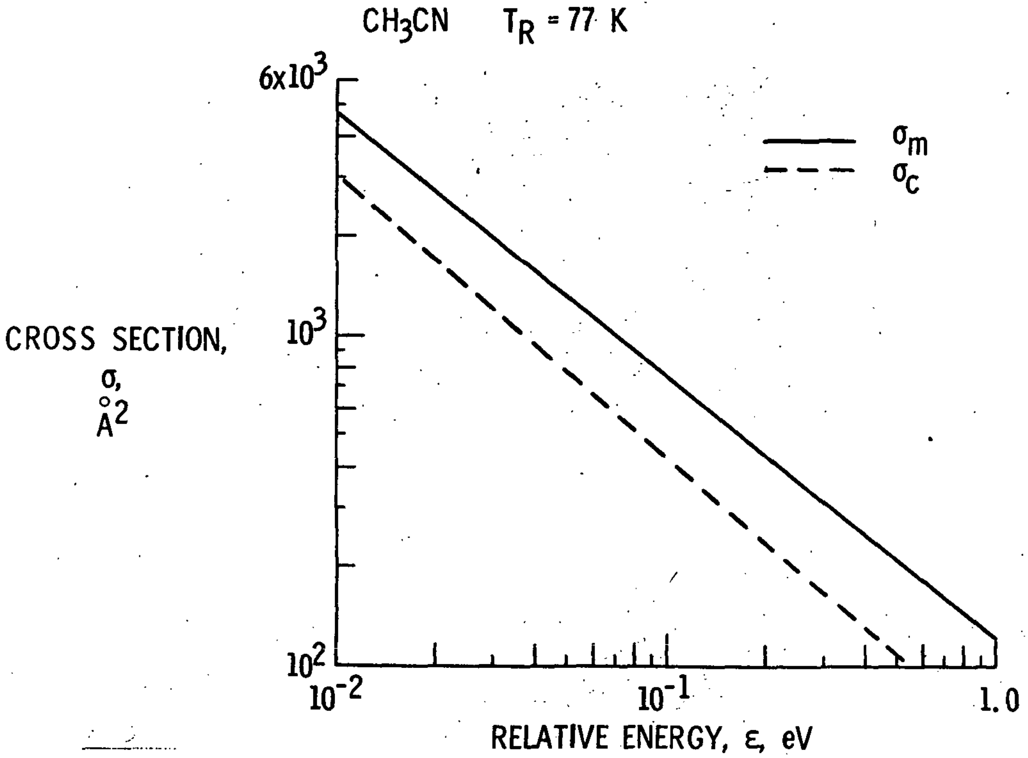


Figure 3. - Variation of momentum transfer and capture cross sections with relative translational energy for ion collisions with CH_3CN targets chosen from a heat bath at rotational temperature of 77 K.

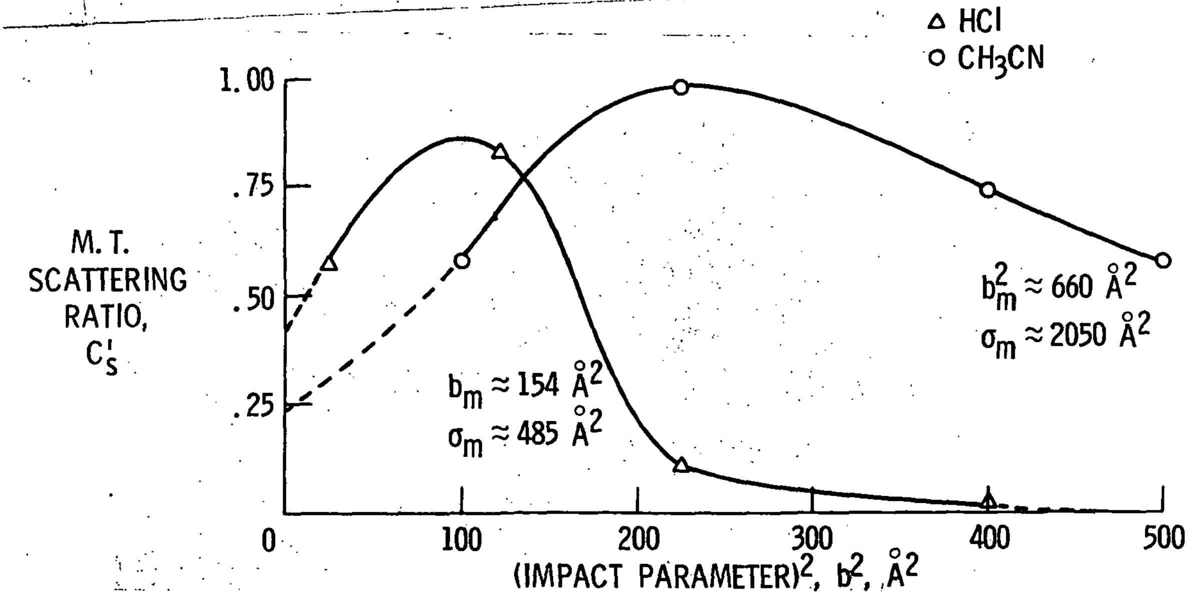


Figure 4. - Comparison of variations of momentum transfer scattering ratios with square of impact parameter for ion collisions at velocity of 5×10^4 cm sec^{-1} with targets having dipole moments of CH_3CN and HCl chosen from bath at $T_R = 77$ K.