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ION-QUADRUPOLE EFFECTS IN ION-MOLECULE COLLISIONS

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ABSTRACT

Ion-quadrupole effects are investigated via numerical calculations of capture cross sections and computer-plotter studies of ion trajectories in the quadrupole field. Capture cross sections are roughly equal to Langevin values for low rotational temperatures; a large fraction of multiple reflection captures are calculated corresponding to formation of ion-molecule complexes.

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INTRODUCTION

The role of the ion-dipole interaction in determining the capture cross section and causing complex formation in ion-molecule collisions has been investigated (refs. 1 to 5). The ion-dipole interaction is an orientation-dependent potential energy term

$$V_D = \frac{-\mu e \cos \gamma}{R^2} \tag{1}$$

where μ is the dipole moment, e is the electronic charge, and R is the ion-molecule separation. The angle γ is the ion-dipole orientation angle between the ion-molecule separation vector $\vec{R}$ and the dipole moment vector $\vec{\mu}$ (taken along the molecular axis). Nonpolar molecules ($\mu \equiv 0$) may still have directional interactions with ions in the classical approximation since they have quadrupole moments. The ion-quadrupole interaction potential is

$$V_Q = \frac{Q_M e(3 \cos^2 \gamma - 1)}{2R^3} \tag{2}$$

where Q_M is the quadrupole moment in (coulomb-m^2) units and γ is the angle between $\vec{R}$ and the molecular axis. The purpose of this paper is to study the effects of the ion-quadrupole interaction on ion-molecule capture cross sections and the formation of collision complexes.

METHOD OF CALCULATION

A classical model is used to devise the equations of motion which are solved numerically using a variable step-size Runge-Kutta integration routine (refs. 1 to 6). The method used is that described in Ref. 6 except the ion-quadrupole term replaces the ion-dipole term in the Lagrangian. The coordinate system used for the calculation is shown in Fig. 1. The equations are solved for nonzero electronic polarizability $(\alpha \neq 0)$ as well as the $\alpha = 0$ case. The former is more realistic, since all molecules of interest have finite electronic polarizabilities. The equations of motion follow from the Lagrangian

$$\bar{L}_Q = \frac{m}{2}\left(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2\right) + \frac{I}{2}\left(\dot{\xi}^2 + \dot{\eta}^2 \sin^2 \xi\right)$$

$$-Q_M e \left\{ \frac{\dfrac{3(X \sin \xi \sin \eta - Y \sin \xi \cos \eta + Z \cos \xi)}{R^2} - 1}{2R^3} \right\} + \frac{\alpha e^2}{2R^4} \tag{3}$$

The form of the translational acceleration term is:

$$X_i = \frac{-Q_M e \left\{ R^2 (6F_\gamma x_i - 2X_i) - 5X_i (3F_\gamma^2 - R^2) \right\}}{mR^7} \tag{4}$$

where X_i $(i = 1, 3) = X$, Y, and Z, $F_\gamma = R \cos \gamma$ and x_i is the Cartesian coordinate of the rotating molecule (where x_1, x_2, and $x_3 = \ell \sin \xi \cos \eta$, $\ell \sin \xi \sin \eta$, $\ell \cos \xi$ with $\ell = 1$). The rotational acceleration terms for the azimuthal and polar angles respectively are:

$$\ddot{\eta} = \frac{-\left\{2\dot{\eta}\xi \cos \xi + Q_M e \left[6 F_\gamma (X \sin \xi \cos \quad + Y \sin \xi \sin \eta)\right]\right\}}{\sin \xi} \tag{5}$$

$$\ddot{\xi} = \dot{\eta}^2 \sin \xi \cos \xi - \frac{Q_M e}{IR^5} \left\{6 F_\gamma (X \cos \xi \sin \eta - Y \cos \xi \cos \eta - Z \sin \xi)\right\} \tag{6}$$

where I is the moment of inertia of the linear target molecule.

Maximum Capture Cross Section

The ion-quadrupole interaction energy has a minimum (i.e., attractive phase) where $\gamma = \pi/2$ and $(V_Q)_{min} = -Q_M e/2R^3$. The maximum cross section corresponding to this optimum orientation can be derived using an effective potential composed of ion-quadrupole and angular momentum terms. This derivation is based on the assumption that the radial velocity $\dot{R}$ is zero at the top of the angular momentum barrier. The effective potential is:

$$V_{eff}(R) = \frac{-Q_M e}{2R^3} + \frac{L^2}{2mR^2} = -\frac{Q_M e}{2R^3} + \epsilon\left(\frac{b}{R}\right)^2 \tag{7}$$

where $L = mvb$ is the translational angular momentum, m is the reduced mass, ϵ is the relative translational energy, and v is the relative speed of ion and molecule and b is the impact parameter. $V_{eff}(R)$ has a single maximum at $R^* = (3Q_M e/4\epsilon b^2)$. This derivation ignores energy transfer; that is, no energy is exchanged between translational and rotational modes. Further, it is assumed that the molecular axis remains at $\pi/2$ to $\vec{R}$; i.e., the rotator is "completely hindered." The maximum effective potential energy is equal to the relative translational energy; i.e., on substituting for R^* in Eq. (7), we can write

$$\left[\left(\frac{4\epsilon b^2}{3Q_M e}\right)^2 \frac{\epsilon b^2}{3}\right]_{R=R^*} = \epsilon \tag{9}$$

On rewriting, we can solve for the critical impact parameter b^*; i.e.

$$(b^*)^6 = \frac{27 Q_M^2 e^2}{16\epsilon^2} \tag{10}$$

and the maximum capture cross section

$$(\sigma_Q)_{max} \equiv \pi b_Q^* = \pi \left(\frac{27\ Q_M^2 e^2}{16\epsilon^2}\right)^{1/3} \tag{11}$$

For N_2 with a quadrupole moment of 1.44×10^{-26} esu-cm^2 (0.48×10^{-39} C-m^2) (ref. 7), Eq. (10) predicts a capture cross section of 102 Å^2 for $\epsilon = kT$ with $T = 300$ K. For the same case the Langevin capture cross section

$$\sigma_L \equiv \pi b_L^2 = \pi\left(\frac{2\alpha e^2}{\epsilon}\right)^{1/2}$$

where α is the electronic polarizability. For N_2 with $\alpha = 1.76$ Å^2 (ref. 8) σ_L is 141Å^2. Since these cross sections are of the same order, it is necessary to consider the quadrupole term in predicting the reaction cross sections at low ion and rotational energies. The average value of $(3\cos^2\gamma - 1)$ during a representative collision remains to be determined from the numerical calculations. Since the ion tends to orient the quadrupole attractively, this value will be less than the average overall orientations, which is zero.

The numerical capture cross section σ_c is calculated from the capture ratio C_R which is the fraction of collisions that reach a prescribed minimum separation R_c. Thus σ_c is simply

$$\pi \int_0^{\infty} C_R(b^2)d(b^2)$$

i.e., π times the integral under the curve of C_R versus b^2. Such a plot is a simple step function at $b = b_L$ for the Langevin case.

Time History Plots

Time history plots of the ion trajectories have been particularly useful in demonstrating the spiraling which results from multiple-reflection behavior with dipole targets (refs. 3 to 5). Similar plots of the ion-quadrupole orientation angle γ versus R are used to demonstrate the hindering alinement along the radius vector of the molecular rotation by the ion field. Plots of planar projections of the ion versus ion-molecule separation R give direct evidence for multiple reflection behavior. A hard-core distance R_c (at which reflection occurs) of 1.5 Å was used in all calculations. This distance, which is one-half the value used for most ion-dipole studies, was chosen because nonpolar molecules generally have smaller characteristic diameters than polar molecules (ref. 8). The variations in magnitude of the relative velocity and molecule rotational energy are used to demonstrate the extent of the energy transfer.

Capture Cross Section

Results of capture ratio versus impact parameter are plotted in Fig. 2 for a molecule of quadrupole moment of 4.15×10^{-39} C-m^2 and zero electronic polarizability ($\alpha = 0$). The results are presented for an ion velocity of 5×10^4 cm sec^{-1} with target rotators chosen from distributions of energies at temperatures T_R of 77 and 300 K. Both capture ratios behave differently than the step function drop off from unity to zero for the Langevin (spherically symmetric polarizability) case. The Langevin C_R plot is for a molecule with relatively large polarizability. The C_R values are less than unity even for a relatively small impact parameter of 5 Å. This indicates that the ion cannot "line up" the quadrupole at the critical turning points in every collision. This is confirmed in Fig. 3 by the plots of orientation angle γ versus ion-molecule separation for a representative repulsion collision. The capture cross sections σ_c are approximately 380 Å^2 and 315 Å^2 for 77 and 300 K.

The nonzero polarizability case is a better approximation to a real molecular system. Results for $\alpha = 3.8$ Å^3 (CH_3CN value) are presented in Fig. 4 and compared with the corresponding Langevin b_L^2 plots. It is clear that the ion-quadrupole term plays a significant role in determining the capture cross section. It does not play its maximum possible role in determining capture as shown by comparison with $(b_Q^2)_{max}$ the capture ratio for the maximum quadrupole contribution. The upper limit value $b_M^2 = (b_Q)^2_{max} + b_L^2$ is also plotted. Just as in the ion-dipole case (refs. 4 and 5), the ion-quadrupole and Langevin potential terms are not simply additive in determining the capture cross section. The results suggest that the ion-quadrupole effect should be investigated experimentally since it may contribute significantly to the reaction cross section for interesting molecular systems (ref. 7).

Multiple-Reflection Results

The variation of the projection of the ion path in the X-Y plane for representative multiple-reflection collisions shows the variation of turning points for the ion-quadrupole case ($\alpha \neq 0$) (see fig. 5). The turning points vary from 3 to 9 angstroms since this potential is effectively shorter range than the ion-dipole where orbiting takes place at separations as large as 23 Å (ref. 5). The maximum number of reflections was set to 5, so many of the trajectories were truncated as reflections continued to occur. Further, roughly 20 percent of the trajectories were truncated (because the step-size chosen became "too small") at the reflection distance, $R \leq R_c$, after at least one capture because the radial acceleration becomes very large. Since the reflection is accomplished by changing the sign of the radial velocity $\dot{R}$, this cannot be accomplished with satisfactory energy conservation if $\ddot{R}\,\Delta t \cong \dot{R}$. Thus, the number of multiple-reflection cases observed is a lower limit and the upper limit is that number plus the "too small" cases. The upper and lower limit figures are presented in Table I. It is clear that the fraction of captures which are multiple-reflection collisions at impact parameters from 5 to 12 Å, is significant for all b values. Many of the collisions are five capture cases, which suggests the possibility of formation of long-lived complexes via the ion-quadrupole potential. Incorporation of vibration (allowing for coupling) in the collision model should provide a more realistic appraisal of the role of this interaction.

An energy transfer in a representative ion-quadrupole capture collision is shown in Figs. 6(a) and 6(b), where relative speed and rotational energy E_R are plotted versus R. The exchange generally takes place at smaller separations than in the ion-dipole case and the maximum values of relative speed and rotational energy are somewhat smaller. Both results are expected on the basis of the relative strength of the potential terms; i.e.,

$$\frac{Q_M e}{2R^3} \text{ versus } \frac{\mu e}{R^2}$$

In view of the considerable energy transfer, it is not surprising that the capture CS results are somewhat less than the "completely hindered" limit.

CONCLUDING REMARKS

The capture ratio results for ion-quadrupole collisions are similar to ion-dipole collisions in that the probability of orienting the rotator is a complicated function of impact parameter.

The role of the ion-quadrupole term in causing multiple reflection behavior (i.e., the formation of ion-molecule collision complexes) is similar to the ion-dipole term. However, the turning points for orbiting are at separations of 2 to 9 angstroms; this behavior is similar to the behavior of weak dipole moment targets like CO.

Since most highly polar molecules have the largest quadrupole moments, the role of this term coupled to the ion-dipole term should be investigated. If the quadrupole moment is considered as a function of vibrational motion, the model could provide additional information about real systems.

REFERENCES

1. J. V. Dugan, Jr. and J. L. Magee, J. Chem. Phys. 47, 3103 (1967).
2. J. V. Dugan, Jr., J. Rice and J. L. Magee, Chem. Phys. Letters 3, 323 (1969).
3. J. V. Dugan, Jr., R. W. Palmer and J. L. Magee, Chem. Phys. Letters 6, 158 (1970).
4. J. V. Dugan, Jr. and R. B. Canright, Jr., Chem. Phys. Letters 8, 253 (1971).
5. J. V. Dugan, Jr. and J. L. Magee, in Advances in Chemical Physics (John Wiley & Sons, New York, 1971), Vol. 21, pp. 207-235.
6. R. B. Canright, Jr. and J. V. Dugan, Jr., NASA TM X-2151 (1971).
7. E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson and L. Friedmand, Ion-Molecule Reactions (Interscience, New York, 1970).
8. J. O. Hinschfelder, C. F. Curtiss and R. B. Byrd, Molecular Theory of Gases and Liquids (John Wiley & Sons, New York, 1964), p. 950.
9. Ref. 8, p. 1028.

TABLE I

[$\alpha = 3.8$ Å^3, $v = 5\times10^4$ cm sec^{-1}]

(a) $T_R = 77$ K

b, Å	[a] $(f_R)_{min}$	$(f_R)_{max}$
6	0.30	0.56
7	.42	.66
8	.18	.60
9	.22	.74
10	.27	.83
11	.36	.88
12	.30	1.00

(b) $T_R = 300$ K

5	0.0	0.21
6	.24	.42
7	.24	.48
8	.24	.64
9	.49	.76
10	.35	.44
11	.63	.83
12	.25	1.00

[a] $f_R = \dfrac{\text{(number of multi. ref.)}}{\text{(number of captures)}}$

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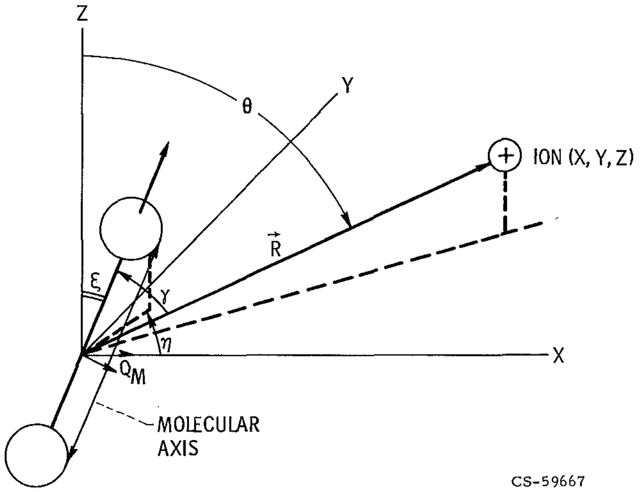

Figure 1. - Coordinate system used in numerical studies of ion-quadrupole effects.

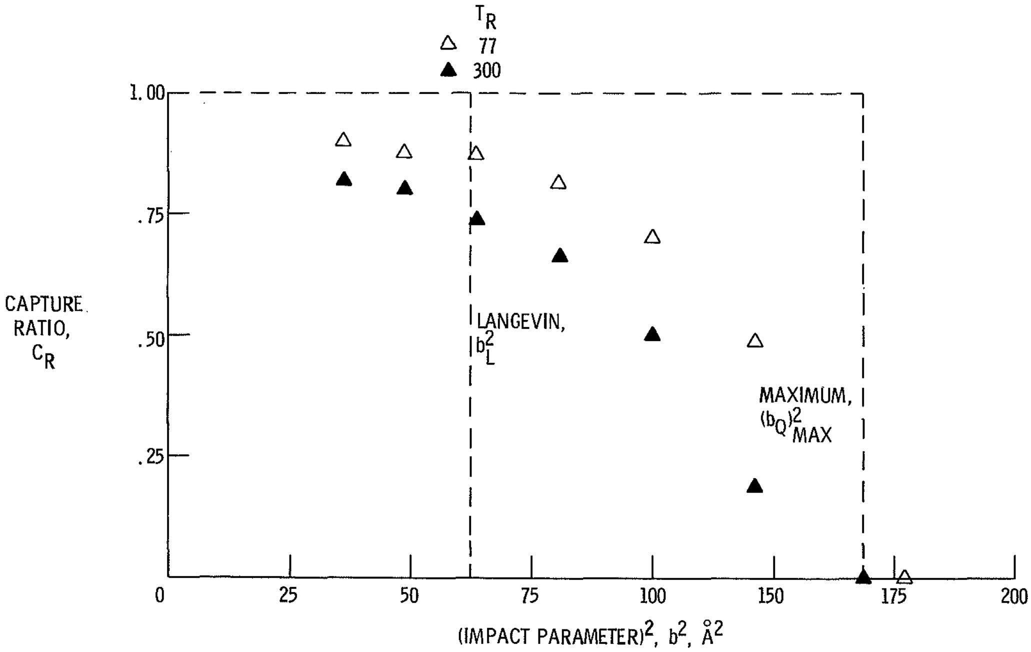

Figure 2. - Plots of numerically calculated capture ratio versus impact parameter for Langevin ion-quadrupole interaction with zero electronic polarizability. Results are compared with the limiting cases. $v = 5\times10^4$ cm sec^{-1}; $\alpha = 0$.

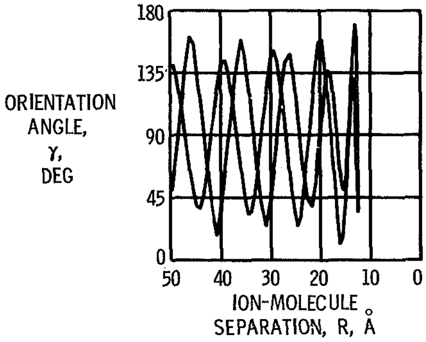

Figure 3. - Orientation angle vs. ion-molecule separation for ion-quadrupole repulsion collision for impact parameter of 6 Å.

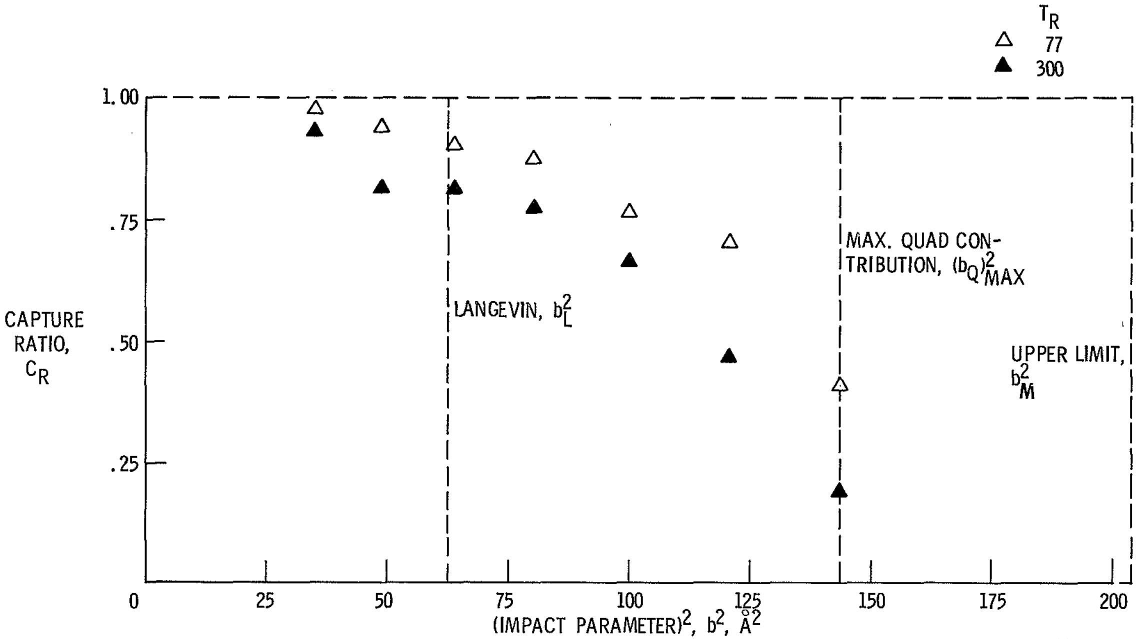

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Figure 4. - Plots of numerically calculated capture ratio versus impact parameter for the ion-quadrupole interaction with finite electronic polarizability. Results are compared with the Langevin and upper limit cases. $v = 5\times10^4$ CM SEC^{-1}; $\alpha \neq 0$.

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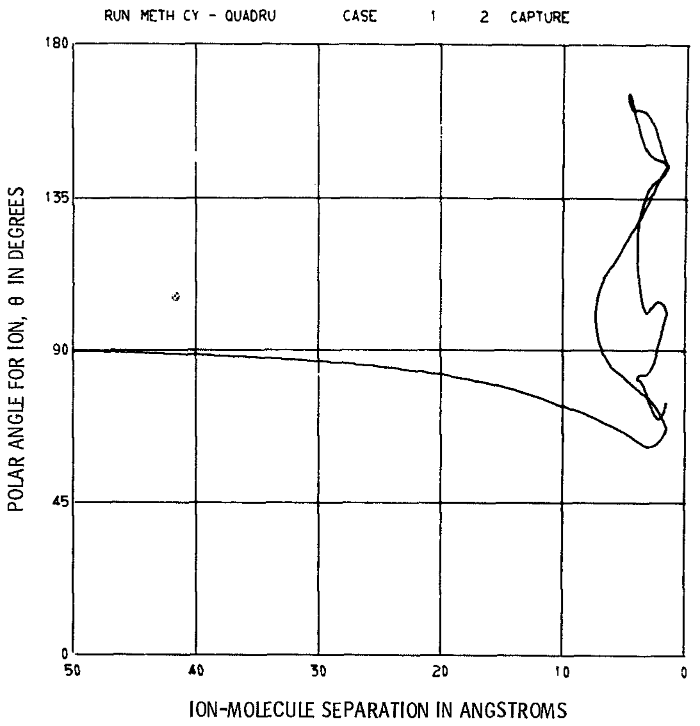

Figure 5. - Variation of polar angle for ion translational motion versus ion-molecule separation for an ion-quadrupole capture collision with five reflections.

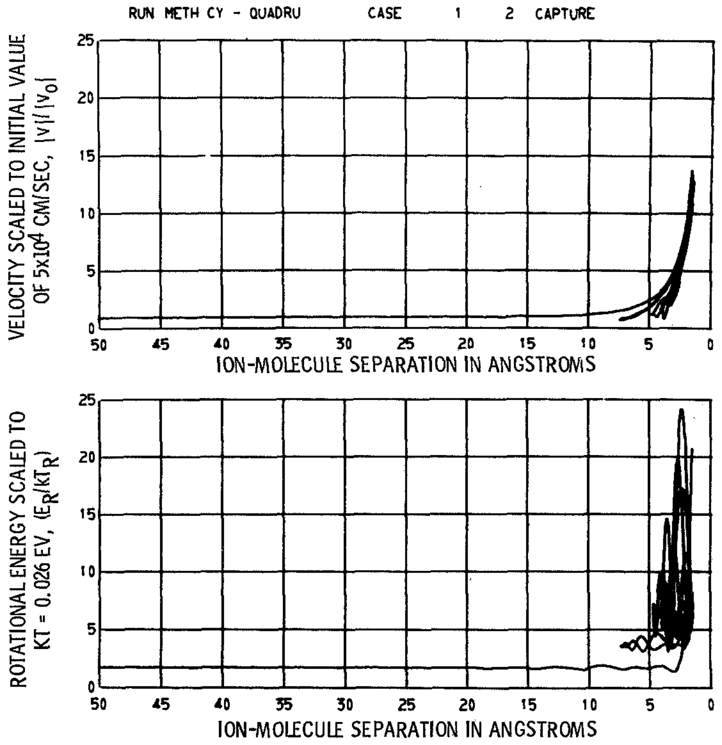

Figure 6. - Variation of scaled values of relative speed and target rotational energy versus ion-molecule separation in an ion-quadrupole multiple reflection capture collision.