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# Dynamics of association and decay. A model study of $\text{Cl}^- + \text{Cl}_2 \rightleftharpoons \text{Cl}_3^-$ using quasiclassical trajectories<sup>a)</sup>

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Quasiclassical trajectories on a model potential-energy surface have been used to study  $\text{Cl}^- + \text{Cl}_2 \rightleftharpoons [\text{Cl}_3]^-$ . Rate coefficients are reported for both the forward and backward processes. Decay rate constants as a function of energy and thermal rate coefficients for forming  $[\text{Cl}_3]^-$  complexes that live for a given number of inner turning points in the  $\text{Cl}^- + \text{Cl}_2$  relative motion are reported.

## I. INTRODUCTION

Termolecular ion-molecule association involving an inert third body M can be written as three elementary processes:



and



The ion  $\text{A}^+$  collides with molecule B to form energetically unstable  $[\text{AB}^+]^*$  which undergoes either a stabilizing collision with M or unimolecular dissociation. Reactions (1) and (2) are the first steps in the clustering of molecules upon a central ion.<sup>1</sup> Ion-molecule clustering is of considerable interest in many areas of chemistry and physics which range from atmospheric to biological processes.

The kinetically important product of the first ion-molecule collision in the termolecular process is a complex that lives sufficiently long that collisional stabilization can occur. Information about such an unstable species, and the processes that create it, is not directly obtainable in the laboratory. However, rates for termolecular association reactions have been measured for various systems using flowing afterglow techniques.<sup>2</sup> Recently, Babcock and Streit<sup>3</sup> reported three-body rate coefficients for  $\text{Cl}_3^-$  formation in helium buffer gas which they measured by using the flowing afterglow technique:



Experimental data for such a simple system provides the impetus to begin the development of a better theoretical understanding of the problem of clustering of molecules upon a central ion. Theoretical studies are needed also to help in analysis of the experimental data since the individual rate coefficients  $k_f$ ,  $k_d$ , and  $k_3$  are not obtained in the experiments; only the overall rate of formation of the stable cluster in the presence of the third body is measured. If the cluster contains a large

number of internal degrees of freedom, various statistical theories may provide an adequate description of the processes.<sup>4</sup> For example, RRKM is probably valid for systems of moderate to large sizes.<sup>5</sup> However, it cannot necessarily be assumed that energy randomization occurs for a complex as small as  $\text{Cl}_3^-$  before it undergoes a collision or unimolecular decay and thus a statistical treatment of reaction (3) is probably not appropriate.

We have carried out quasiclassical trajectory calculations for collisions of  $\text{Cl}^-$  with  $\text{Cl}_2$  using a model potential-energy surface. We have selected a simple model for this initial study of ion-molecule clustering. The potential-energy surface is a crude model and is probably not a realistic representation of the forces in  $\text{Cl}_3^-$ . The potential is purely attractive as appropriate for ion-molecule (and van der Waals) systems. The forces are strictly pairwise additive in our model and the well-depth and the location of the well for the  $\text{Cl}^- \cdots \text{Cl}_2$  interaction are, at best, rough estimates. Nevertheless, the model should serve to demonstrate some of the important features of the dynamics of ion-molecule association reactions. We are interested in the general problem of complex formation and decay. Our purpose in the present study was to determine some of the general, fundamental properties of the dynamics of association and dissociation which serve as the initial steps of heterogeneous nucleation, and in the case of association, as the precursor to chemical reaction in ion-molecule chemistry. The present study is a fairly detailed treatment of ion capture. We present a definition of capture in which the lifetime of the complex is taken into account and show that simple functional forms can be used to describe the capture. Furthermore, we compute decay rate constants for the complex. The decay is shown to be exponential in time.

Much of the interest in ion-molecule clustering has been concerned with the nonkinetic properties of water-ion systems.<sup>2</sup> Kebarle and co-workers<sup>6</sup> have made extensive experimental studies of the thermodynamics of ions interacting with molecules for a wide variety of systems. And, as mentioned above, kinetics data have been measured using flowing afterglow techniques.<sup>2</sup> These experimental studies have contributed significantly to our understanding of association reactions. However, there remains much to be learned about the details of the reactions. In a collision between an ion and a non-polar molecule the Langevin theory<sup>7</sup> gives an upper

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bound for the capture rate. This theory however is merely a model and the capture rate is of limited usefulness.<sup>8</sup> The Langevin theory describes trajectories which undergo a collision with the repulsive wall, i.e., those which cross the centrifugal barrier for the collision. Dugan and co-workers<sup>9</sup> carried out a number of classical trajectory calculations that extensively explored ion capture. More recently, Chesnavich, Su, and Bowers<sup>10</sup> have carried out some excellent studies of ion capture using variational rate theory and classical trajectory methods. Hase and co-workers<sup>11</sup> recently reported classical trajectory studies of collisions of alkali ions with water. We hope to shed additional light on the problem of the encounter of an ion and a molecule with the present study.

## II. COMPUTATIONAL PROCEDURES

The purpose of the present study is to provide a detailed description of the dynamics of the formation and decay of energetically unstable complexes in a simple ion-molecule system. Thus, we have not attempted an accurate study of the real  $\text{Cl}^- + \text{Cl}_2$  system but instead have investigated a model system that has some of the characteristics of the  $\text{Cl}^- + \text{Cl}_2 \rightleftharpoons [\text{Cl}_3]^*$  system. In this section we describe the model used to represent the  $\text{Cl}_3^-$  potential-energy surface and the quasiclassical trajectory methods.

### A. Potential-energy surfaces

There is little information available on the potential-energy surface of  $\text{Cl}_3^-$ . In 1951, Pimentel<sup>12</sup> published the results of a simple molecular orbital treatment of the bonding in trihalides that predicted  $\text{Cl}_3^-$  to be linear. Subsequent experimental studies have also shown the geometry to be linear.<sup>13,14</sup> Robbani and Franklin<sup>15</sup> have estimated, from experimental data, the heat of formation to be  $-3.11$  eV. Tasker<sup>16</sup> has carried out a valence-bond, pseudopotential calculation for  $\text{X}_3^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ); he obtained  $1.69$  eV for the energy to dissociate  $\text{Cl}_3^-$  to  $\text{Cl}_2$  and  $\text{Cl}^-$ .

We have constructed a model potential-energy surface by taking the sum of pair potentials,

$$V(r_1, r_2, r_3) = \sum_{i=1}^3 V_M(r_i), \quad (5)$$

where  $V_M$  is the Morse function,

$$V_M(r_i) = D\{1 - \exp[-\alpha(r_i - r_e)]\}^2 - D. \quad (6)$$

The values of Morse parameters are given in Table I. The  $\text{Cl}_2$  is treated as the isolated molecule. The potential for the  $\text{Cl} \cdots \text{Cl}^-$  pair is based on the *ab initio* calculation of Gilbert and Wahl.<sup>17</sup> We have arbitrarily modified the Gilbert and Wahl potential by multiplying the value of  $D$  they computed for  $\text{Cl}_2^-$  by a half to give the total dissociation energy as  $1.06$  eV for  $\text{Cl}^- \cdots \text{Cl}_2 \rightarrow \text{Cl}^- + \text{Cl}_2$ .

### B. Trajectory calculations

Each trajectory was initiated in the  $\text{Cl}^- + \text{Cl}_2$  limit by taking the separation between the  $\text{Cl}^-$  and the center-of-mass of  $\text{Cl}_2$  to be  $30.0$  a.u. All of the calculations were

TABLE I. Potential parameters.

Parameter	$\text{Cl}_2^a$	$\text{Cl}_2^-^b$
$D$ (eV)	2.51	0.53
$\alpha$ (a.u. <sup>-1</sup> )	1.076 96	0.699 69
$r_e$ (a.u.)	3.757	5.0

<sup>a</sup>From R. N. Porter, L. B. Sims, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 58, 2855 (1973).

<sup>b</sup>Adapted from Gilbert and Wahl, Ref. 17.

carried out for  $\text{Cl}_2$  in the ground vibrational-rotational state; the molecule initially possessed zero-point vibrational energy. The initial vibrational phase of  $\text{Cl}_2$  was selected by using the Porter, Raff, and Miller<sup>18</sup> procedure. The maximum impact parameter was  $8.0$  a.u.

We computed both the cross section as a function of lifetime for the formation of the energetically unstable  $\text{Cl}_3^-$  and the decay rate constant for its dissociation. These quantities are, of course, measurements of the same dynamical properties, however, it is informative to consider both. Three classes of calculations were carried out: (1) Collinear collisions as a function of the initial relative translational energy, (2) collisions without restrictions on the motion as a function of the impact parameter and initial relative translational motion, and (3) collisions in which all the collision variables except the initial relative translational energy were Monte Carlo averaged.

Each trajectory was integrated, starting with the  $\text{Cl}^- \cdots \text{Cl}_2$  distance equal to  $30$  a.u., until the  $\text{Cl}^-$  was again separated from the  $\text{Cl}_2$  center-of-mass by that distance. If the ion had not escaped the molecule by that distance after  $3.3 \times 10^{-11}$  s trajectory time had elapsed the trajectory was terminated. This time limit on the trajectory integration is such that at least 90% of the trajectories were not terminated by the time-limit cutoff for the lowest collision energy studied ( $0.1$  eV), and in most cases no trajectories were thus ended. The lifetime of an individual complex was defined as the trajectory time which elapsed between the first and last inner turning points in the motion of the  $\text{Cl}^-$  relative to the  $\text{Cl}_2$  center-of-mass.<sup>19</sup> Thus, those trajectories in which there was a single minimum in the separation of  $\text{Cl}^-$  and the  $\text{Cl}_2$  center-of-mass were assigned a lifetime of zero. This procedure removes the time required for the initial encounter of  $\text{Cl}^-$  and  $\text{Cl}_2$ , which varies with the initial relative translational energy, and the time required for the escape of the products to "infinite" separation, which depends on the final relative translational energy.

As will be shown below, the distribution of complex lifetimes have the form

$$\ln(N_t/N_0) = -k_d t, \quad (7)$$

where  $N_t$  is the number of complexes that live for time  $t$  and  $N_0$  is the total number of trajectories. The decay constant  $k_d$  is obtained by computing the slope of the straight line defined by a plot of  $\ln(N_t/N_0)$  vs  $t$ .

Since  $[Cl_3]^*$  is energetically unstable a definition of a formation rate or cross section must depend on the lifetime of the complex. Cross sections for the formation of complexes were computed as a function of the number of inner turning points  $N_{tp}$  of the "vibration" of the  $Cl^-$  with respect to the center-of-mass of the  $Cl_2$ . The turning points counted were those experienced by the complex prior to dissociation or termination of the trajectory by the end-test time limit. The information thus computed is fundamentally the same as that given by the decay curves, Eq. (7); because of microscopic reversibility the rate of change of the formation and dissociation probabilities with the complex lifetime must be the same. However, the magnitude of the cross section for forming a complex of a given lifetime is information not given by the decay curves.

The trajectories were integrated by using a fourth-order Runge-Kutta-Gill routine with a fixed stepsize of  $5.387 \times 10^{-18}$  s. Integration accuracy was checked by back integration, constancy of total energy, and by computing decay constants using various values of the stepsize.

### III. RESULTS AND DISCUSSION

The main interest in this study is the fundamental properties of the long-lived collisions of an ion with a neutral diatomic molecule. As implied by the commonly used notation for such a collision [Eq. (3)], we view the collision as taking place in two steps, collisional formation and unimolecular dissociation of the energetically unstable complex. We study these steps by initiating trajectories in the limit of separated  $Cl^- + Cl_2$  and following them through the formation of a  $[Cl_3]^*$  complex to the dissociation of that complex. We begin our discussion of the results of the trajectory calculations by presenting some plots of individual trajectories.

Since the  $[Cl_3]^*$  complex is energetically unstable, we must define its existence on the basis of its lifetime.

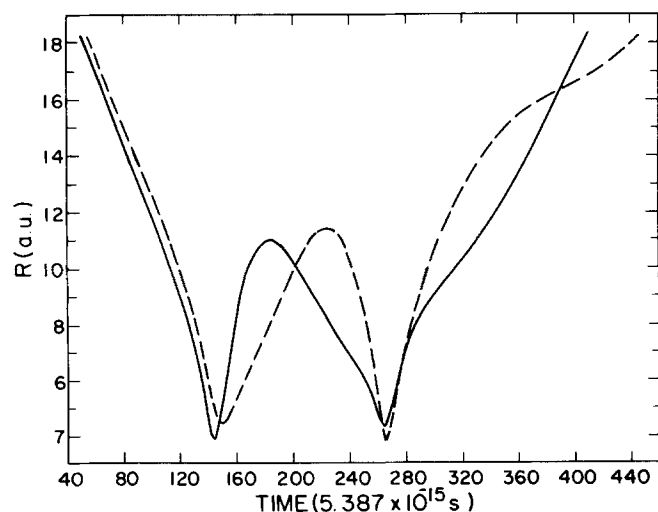


FIG. 1. Plots of the  $Cl^- \cdots Cl$  internuclear separations for a  $Cl^- + Cl_2$  short-lived collision complex as a function of trajectory time. The initial relative translational energy equals 0.2 eV and the impact parameter is 2.0 a.u.

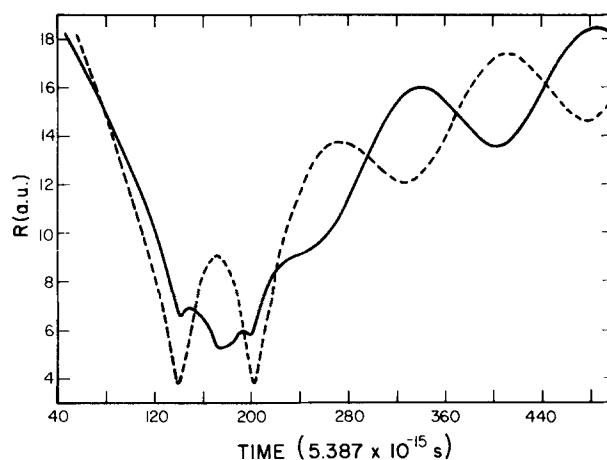


FIG. 2. Same as Fig. 1.

This lifetime must be defined by spatial proximity. A reasonable geometric parameter for this purpose is the inner turning point of the  $Cl^-$  separation relative to the  $Cl_2$  center-of-mass. The most probable type of collision is one in which only one inner turning point is experienced before the ion and molecule separate. These direct collisions are not of interest here. The simplest complex is one in which the  $Cl^- \cdots Cl_2$  separation undergo two inner turning points and then separate. These collisions are the most probable after the direct ones. Figures 1 and 2 show plots of two such trajectories. In these figures we have plotted the two  $Cl^- \cdots Cl$  distances rather than the  $Cl^- \cdots Cl_2$  center-of-mass separation because the nature of the collision is better demonstrated this way. The trajectories in Figs. 1 and 2 are for the initial relative translational energy equal to 0.2 eV and an impact parameter of 2.0 a.u. Both are quite simple collisions. The one plotted in Fig. 1 has a lifetime of about  $6.5 \times 10^{-13}$  s and the one in Fig. 2 lives for  $3.8 \times 10^{-13}$  s, where the lifetime is defined as the time between the first and last inner turning points. In Fig. 3 part of a trajectory with the same energy and impact parameter is plotted. This trajectory does not dissociate before the arbitrary time-limit cutoff of  $3.23 \times 10^{-11}$  s is imposed. The initial part of the trajectory is similar to the short-lived trajectories in Figs. 1 and 2. However, energy is soon transferred from the  $Cl^- \cdots Cl_2$  motion to the  $Cl_2$  internal motion and the complex be-

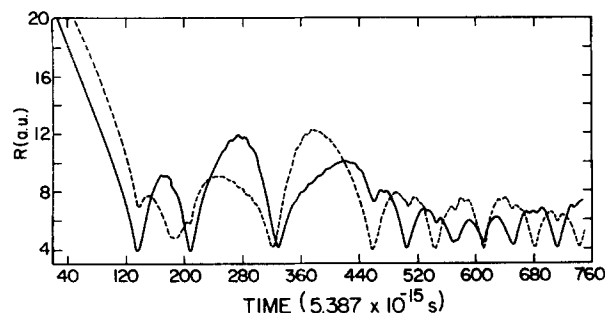


FIG. 3. Same as Fig. 1 except for a long-lived complex which does not dissociate in  $3.23 \times 10^{-11}$  s. Only the initial part of the trajectory is plotted.

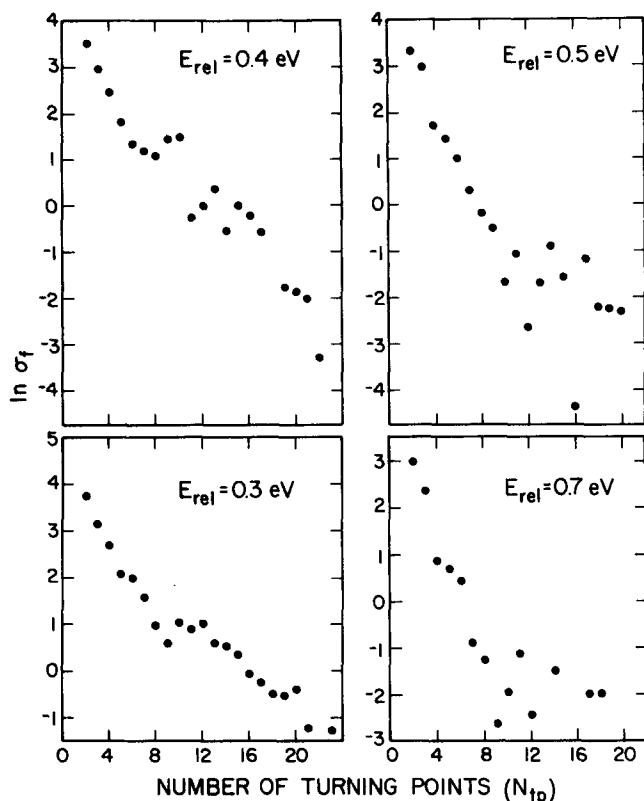


FIG. 4. Plots of the natural logarithm of the cross sections for forming a  $[\text{Cl}_3]^*$  complex in a  $\text{Cl}^- + \text{Cl}_2$  collision that lives for  $N_{\text{tp}}$  inner turning points of the  $\text{Cl}^-$  motion relative to the  $\text{Cl}_2$  center-of-mass as functions of  $N_{\text{tp}}$ . Results are plotted for initial relative translational energies 0.3, 0.4, 0.5, and 0.7 eV.

comes quasistable—the type of motion shown in the latter part of the plot continues to the end of the trajectory at  $3.32 \times 10^{-11}$  s. Eventually, of course, energy will flow back into the dissociative mode and the complex will break up.

We computed the cross section for complex formation  $\sigma_f$  as a function of the number of inner turning points in the motion of the  $\text{Cl}^-$  relative to the  $\text{Cl}_2$  center-of-mass. Typical results are shown in Fig. 4 where  $\ln \sigma_f$  is plotted against the number of turning points for  $E_{\text{rel}} = 0.3, 0.4, 0.5$ , and  $0.7$  eV. The cross section for complex formation is exponentially dependent on lifetime (the number of turning points). This is demonstrated by the linear behavior of the points in Fig. 4. The nonlinearity for the regions of large numbers of turning points is due to poor statistics. As will be shown below, the  $[\text{Cl}_3]^*$  complexes decay with random lifetimes. The results in Fig. 4 also show that the lifetimes are random.

Hase and Feng<sup>11(a)</sup> used classical trajectories to compute the cross section for forming  $[\text{Li}^+(\text{H}_2\text{O})]^*$  in  $\text{Li}^+ + \text{H}_2\text{O}$  collisions. They defined the  $[\text{Li}^+(\text{H}_2\text{O})]^*$  complex as one that lived for more than one inner turning point in the  $\text{Li}^+ + \text{H}_2\text{O}$  relative motion.<sup>11(a)</sup> They refer to the cross section for forming such a complex as the *primary reactive cross section*. They found that this cross section, which we will refer to as  $\sigma_f^{\text{tot}}$ , is ex-

TABLE II. Values of the parameters  $a$  and  $b$  for the cross section model Eq. (8) obtained by least-squares fitting the trajectory results and values of the rate coefficient at 300 K for complexes that live 2, 3, ..., 6 and more than one inner turning points in the  $\text{Cl}^- + \text{Cl}_2$  relative motion.

$N_{\text{tp}}$	$a$ (a. u. <sup>2</sup> )	$b$ (eV <sup>-1</sup> )	$k$ (cm <sup>3</sup> /molecules s)
2	75.846	2.171	$0.99 \times 10^{-10}$
3	36.874	1.625	$0.49 \times 10^{-10}$
4	24.926	2.136	$0.32 \times 10^{-10}$
5	24.697	3.458	$0.30 \times 10^{-10}$
6	20.328	3.860	$0.24 \times 10^{-10}$
>1	254.7	2.737	$3.22 \times 10^{-10}$

ponentially dependent on  $E_{\text{rel}}$ , i. e., their results are well described by the Sorbie–Murrell<sup>20</sup> model

$$\sigma_f^{\text{tot}} = a \exp(-b E_{\text{rel}}). \quad (8)$$

The total cross section is simply the sum of the individual  $\sigma_f$  values plotted in Fig. 4. Figure 5 shows a plot of  $\sigma_f^{\text{tot}}$  against  $E_{\text{rel}}$  for  $\text{Cl}^- + \text{Cl}_2 \rightarrow [\text{Cl}_3]^*$ . The solid line in Fig. 5 was obtained by a least squares fit of the points. The values obtained for the parameters in Eq. (8) are given in Table II. Equation (8) was first used by Murrell and co-workers<sup>20</sup> to fit trajectory results for  $\text{C} + \text{O}_2$  and  $\text{O} + \text{H}_2$ .

The cross sections for forming a complex that experiences a given number of inner turning points in the  $\text{Cl}^- + \text{Cl}_2$  motion also obey Eq. (8). This is illustrated by the cross section values for forming complexes that experience 3, 4, and 5 inner turning points that are plotted in Fig. 6 as a function of the initial relative translational energy. The solid lines are least-squares fits to the cross section values. The values of the parameters  $a$  and  $b$  of Eq. (8) are given in Table II.

An analytical expression can be obtained from the Sorbie–Murrell cross section model [Eq. (8)] for the

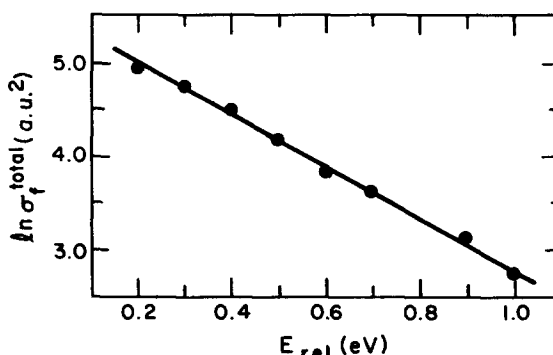


FIG. 5. Plot of the logarithm of the cross section for forming a  $[\text{Cl}_3]^*$  complex in a  $\text{Cl}^- + \text{Cl}_2$  collision that lives for more than one inner turning point in the  $\text{Cl}^- + \text{Cl}_2$  relative motion as a function of the initial relative translational energy. The solid line is a least-squares fit of the points.

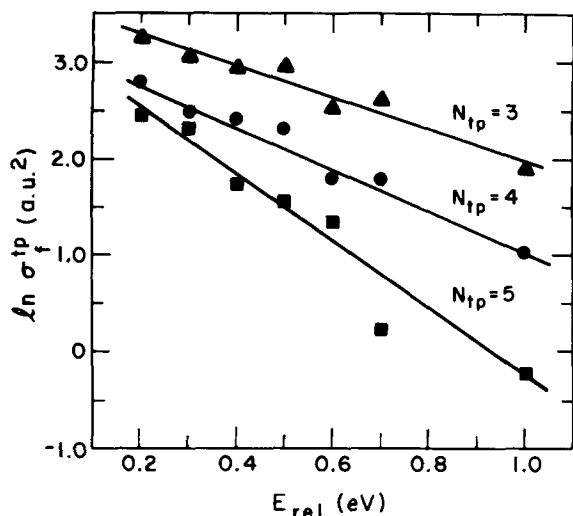


FIG. 6. Plots of the logarithm of the cross sections for forming  $[\text{Cl}_3]^*$  complexes in  $\text{Cl}^- + \text{Cl}_2$  collisions that live for 3, 4, and 5 inner turning points in the  $\text{Cl}^- + \text{Cl}_2$  relative motion as a function of the initial relative translational energy. The solid lines are least-squares fits of the points.

thermal rate coefficient by simply integrating it over the Maxwell-Boltzmann velocity distribution.<sup>20</sup> The thermal rate coefficient for the model is

$$k(T) = (\pi\mu)^{-1/2} (2/\kappa T)^{3/2} a(b + 1/\kappa T)^{-2}. \quad (9)$$

Table II lists the values of the parameters  $a$  and  $b$  of Eq. (8) for  $N_{tp}=2$  to 6 and for all  $N_{tp}$  greater than one. These values of  $a$  and  $b$ , given in columns two and three of the table, were obtained by least-squares fitting of the trajectory results. The values of the rate coefficient computed by Eq. (9) are given in the last column of Table II for  $T=300$  K.

Collisions of an ion and a molecule are usually assumed to be described by the Langevin model.<sup>7,8</sup> Here it is assumed that a collision complex results from ion-induced-dipole attraction. The Langevin theory gives the cross section (or rate coefficient) for forming a "complex" defined as a trajectory in which the effective radial potential centrifugal barrier is crossed. Thus, it describes those trajectories that experience at least one encounter with the inner wall of the potential between the ion and molecule. The Langevin model generally predicts a capture rate coefficient on the order of  $10^{-9}$  cm<sup>3</sup>/molecule s. Of the quantities we have computed using trajectories, the rate coefficient for  $N_{tp}>1$  is the most comparable to the commonly used Langevin definitions of a complex. We obtained a value of  $3.22 \times 10^{-10}$  cm<sup>3</sup>/molecule s for the rate coefficient for forming a complex that lives for more than one inner turning point. This is smaller than one would expect from a Langevin treatment, but is in reasonable agreement considering the details of the methods. Our rate coefficient should be smaller since our definition requires that the complex live at least two inner turning points while the Langevin model requires only one encounter of the ion and molecule. Furthermore, the model po-

tential-energy surface which we have used in the trajectory calculations very likely underestimates the range of attraction expected in collisions governed by ion-induced-dipole forces as assumed in the Langevin theory. This too would cause the trajectory result to be smaller than the Langevin value. Hase and Feng<sup>11</sup> used a realistic potential in their study of  $\text{Li}^+ + \text{H}_2\text{O}$  and their computed rate coefficients are on the order of those expected on the basis of Langevin theory; their computed values range from  $3.78 \times 10^{-9}$  to  $1.08 \times 10^{-9}$  cm<sup>3</sup>/molecule s over the temperature range 200–1000 K.

Table II also includes values of the rate coefficients for forming complexes that live for 2, 3, ..., 6 inner turning points. The rate coefficient decreases as the lifetime of the complex (the number of turning points) increases. The most probable complex,  $N_{tp}=2$ , is formed with a rate coefficient of  $10^{-10}$  cm<sup>3</sup>/molecule s. The rate coefficient for forming the  $N_{tp}=6$  complex is one-quarter of that.

The temperature dependence of the rate coefficient predicted by the Sorbie-Murrell model is illustrated by the plots in Fig. 7 for  $N_{tp}>1$  and  $N_{tp}=3$ . There is an initial rise, relatively sharp in the  $N_{tp}>1$  case, and then a leveling off at high temperature.

Decay curves for the dissociation of  $[\text{Cl}_3]^*$  were obtained by following  $\text{Cl}^- + \text{Cl}_2$  trajectories from reactants to products ( $\text{Cl}^- + \text{Cl}_2$ ) and recording the lifetimes of the complex. The lifetime of a complex was taken to be the trajectory time that elapsed between the first and last occurrence of an inner turning point of the  $\text{Cl}^- + \text{Cl}_2$  relative motion. Collisions in which only one such inner turning point was experienced were assigned a complex lifetime of zero. From an ensemble ( $N_0$  trajectories) of computed lifetimes the probability for a complex of lifetime  $t$ ,  $N_t/N_0$ , was obtained. A plot of the natural

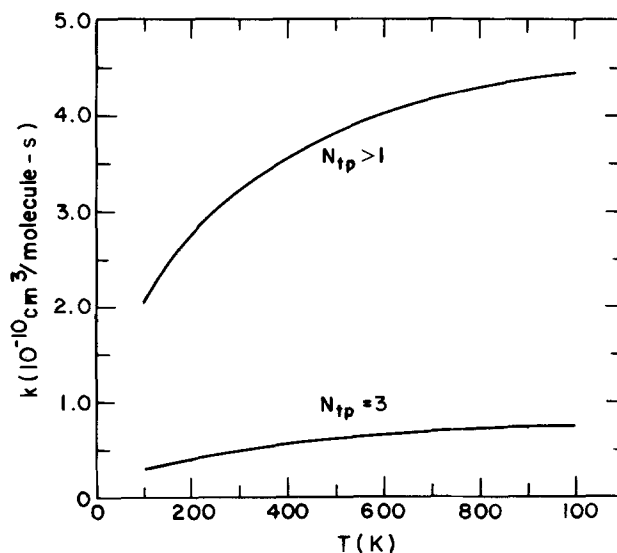


FIG. 7. Plots of the thermal rate coefficients for forming  $N_{tp}>1$  and  $N_{tp}=3$  complexes in  $\text{Cl}^- + \text{Cl}_2$  collisions as a function of temperature. The curves are predicted by Eq. (9).

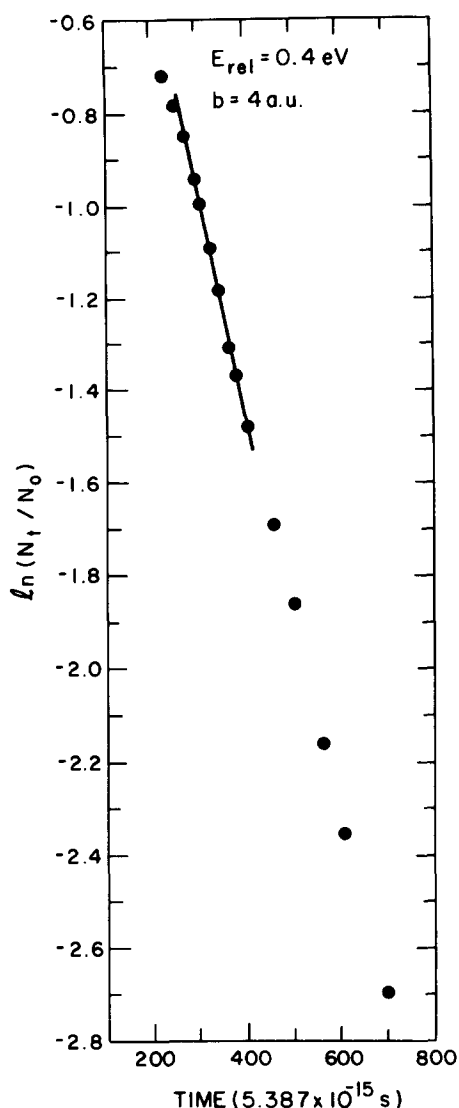


FIG. 8. Decay curve for  $\text{Cl}^- + \text{Cl}_2 \rightleftharpoons [\text{Cl}_3]^*$  with fixed energy ( $E_{\text{rel}} = 0.4$  and  $0.035$  eV initial zero-point vibrational energy in  $\text{Cl}_2$ ) and fixed impact parameter ( $b = 4$  a.u.). This plot is for an ensemble of 400 trajectories.

logarithm of  $N_t/N_0$  as a function of  $t$  at fixed energy yields a straight line, the slope of which is the decay rate constant  $k_d$ . Angular momentum need not be held constant in these calculations because of its weak influence.

Figure 8 shows a typical decay curve for fixed energy ( $E_{\text{rel}} = 0.4$  eV) and fixed impact parameter ( $b = 4$  a.u.). A decay curve for  $E_{\text{rel}} = 0.3$  eV in which the impact parameter was averaged over the range  $0 \leq b \leq 8$  a.u. is shown in Fig. 9. In both cases the points fall on a line. The exponential decay law [Eq. (7)] is well obeyed. As can be seen from Figs. 8 and 9, the degree of linearity is hardly affected by averaging over angular momentum (impact parameters). We also found this to be the case in studies of rare gas clusters.<sup>21</sup>

Figure 10 shows a plot of the decay rate constant as a function of impact parameter for  $E_{\text{rel}} = 0.4$  eV. The most striking feature of this plot is that  $k_d$  is relatively

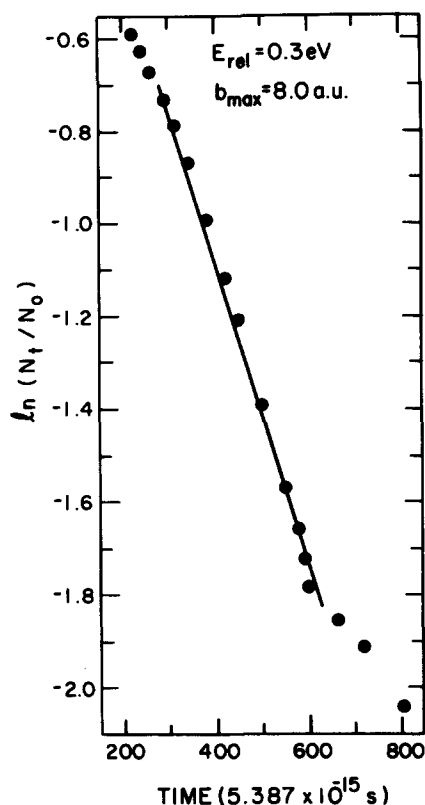


FIG. 9. Decay curve for  $\text{Cl}^- + \text{Cl}_2 \rightleftharpoons [\text{Cl}_3]^*$  with fixed energy ( $E_{\text{rel}} = 0.3$  and  $0.035$  eV initial zero-point vibrational energy in  $\text{Cl}_2$ ). Impact parameters were averaged over the range  $0 \leq b \leq 8$  a.u. This plot is for an ensemble of 500 trajectories.

invariant with changes in  $b$  over a wide range. At very large  $b$  ( $\sim 8$  a.u.) the rate constant increases rapidly. We have arbitrarily taken 8 a.u. for the maximum allowed value for the impact parameter in the calculations in which it is Monte Carlo averaged.

Figure 11 shows a plot of the dissociation rate constant as a function of the initial relative translational

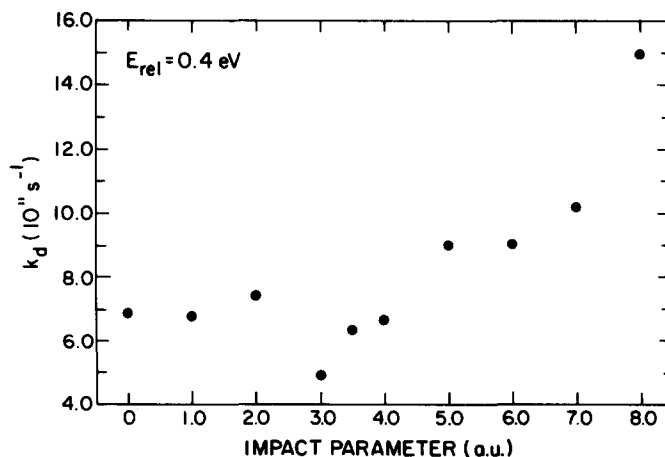


FIG. 10. Plot of the decay rate constant  $k_d$  as a function of impact parameter for  $E_{\text{rel}} = 0.4$  eV ( $\text{Cl}_2$  initially has  $0.035$  eV zero-point vibrational energy).

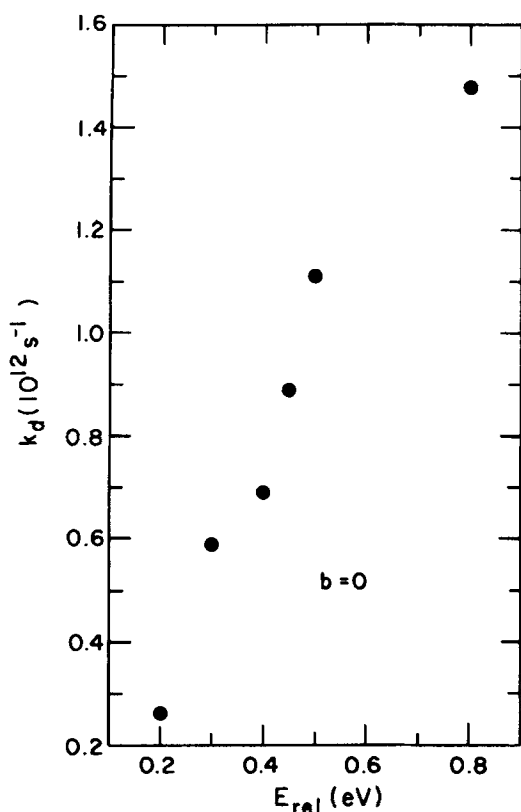


FIG. 11. Plot of the decay rate constant as a function of the initial relative translational energy for zero impact parameter collisions. The total energy of the system is  $E_{rel}$  plus 0.035 eV zero-point vibrational energy for  $Cl_2$ . The initial orientation of the  $Cl_2$  in the  $Cl^- + Cl_2$  collisions is random.

energy for zero impact parameter collisions. The molecular orientation in the collisions was random. Thus, these results are for three-dimensional motion with zero angular momentum. The value of  $k_d(E)$  rises rapidly as  $E_{rel}$  (the total energy is  $E_{rel}$  plus 0.035 eV  $Cl_2$  zero-point vibrational energy) increases. Figure 12 shows a plot of  $k_d(E)$  as a function of  $E_{rel}$  for completely general collisions where the impact parameter was averaged over the range  $0 \leq b \leq 8$  a.u. The general behavior of the results in Fig. 12 is the same as that for those plotted in Fig. 11. Angular momentum has a negligible influence on the value of  $k_d(E)$ .

#### IV. SUMMARY AND CONCLUSIONS

A quasiclassical trajectory study has been carried out for the formation and decay of energetically unstable  $[Cl_3]^*$  complexes formed in  $Cl^- + Cl_2$  collisions. A model potential-energy surface using pairwise forces was employed. The purpose in the present work was to elucidate some of the fundamental properties of the dynamics of association and dissociation in ion-molecule collisions. The process studied is a model of the initial step of molecular clustering upon a central ion.

We have computed cross sections for forming  $[Cl_3]^*$  complexes as a function of the complex lifetime (the number of inner turning points in the  $Cl^- + Cl_2$  relative motion was used as a measure of complex lifetime).

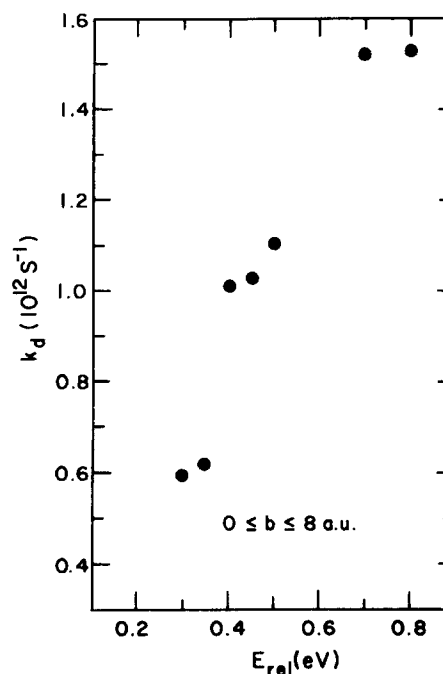


FIG. 12. Plot of the decay rate constant as a function of the initial relative translational energy for impact parameters averaged over the range  $0 \leq b \leq 8$  a.u. The total energy of the system is  $E_{rel}$  plus 0.035 eV zero-point vibrational energy for  $Cl_2$ .

The cross section values obtained from the trajectory calculations were then fit using the Sorbie-Murrell<sup>20</sup> model. Thermal rate coefficients were computed using the analytical expression for this model. The rate coefficients thus computed are somewhat smaller than those normally quoted for ion-molecule reactions on the basis of Langevin theory.

Decay rate constants as a function of both the initial relative translational energy and the impact parameter and as a function of only the initial relative translational energy were computed from the trajectories. The trajectory results show that  $[Cl_3]^*$  decays with random lifetimes.

<sup>1</sup>For an interesting and comprehensive discussion of the problem of clustering upon a central ion, see: A. W. Castleman, Jr., in *Kinetics of Ion-Molecule Reactions*, edited by P. Ausloos (Plenum, New York, 1979), p. 295.

<sup>2</sup>See, for example, D. Smith and N. G. Adams, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. 1, p. 1.

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<sup>4</sup>For a review of statistical treatments see, W. J. Chesnavich and M. T. Bowers, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. 1, p. 119.

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