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Trajectory calculations of relative center of mass velocities in collisions between Ar and toluene

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Average velocities of Ar relative to the center of mass of toluene in bimolecular collisions were determined using quasiclassical trajectory calculations. The collision durations were binned in 20 fs and 100 fs bins and for each bin the velocities of all trajectories were averaged. 10 000 trajectories were calculated. About 64% of all collisions were elastic and the rest were inelastic collisions. The remaining 36% inelastic collisions can be classified into four types. (a) Impulsive collisions of duration 0–300 fs (62%). (b) Chattering collisions of duration longer than 300 fs but shorter than intramolecular vibrational relaxation (IVR) times ($>30\%$). (c) Complex forming collisions which last longer than molecular IVR times but less than complex (molecular+transition modes) IVR times and complex forming collisions which last longer than complex IVR times. The latter may lead to statistical distribution of energy in the collision complex. These long lived trajectories have negligible contribution to the value of the average energy transferred. (d) Supercollisions (0.12%) which are collisions which transfer an inordinate amount of energy in one event. The details of the collisional process are discussed and sample distributions are presented. Analysis of the collision events indicate that out-of-plane vibrations and overall rotations play a major role in the energy transfer mechanism. A comparison with existing analytical energy transfer models is presented and it is shown that some of them do not agree with the present trajectory calculation results. It is suggested that supercollisions in the gas phase and in solution play a major role in chemical reactions. © 1996 American Institute of Physics. [S0021-9606(96)02005-X]

I. INTRODUCTION

Photophysical phenomena and chemical reactions in the gas phase are intimately dependent on intermolecular energy transfer. Collisions are the vehicle by which energy is removed from highly excited molecules and energy is supplied, by an up-pumping process, to cold molecules enabling them to emit or react. Thus, understanding collisional energy transfer is prerequisite to a quantitative understanding and interpretation of photophysical processes and thermal and photochemical reactions.

Lindemann's realization in the early twenties that collisions play an integral part in unimolecular reactions initiated a continuous preoccupation with the contribution of collisions to chemical reaction. Lindemann's model of a two level system whereby the reactant molecules are either excited or not and are transported from one level to the other by a single collision was used in early unimolecular theories. This notion of an efficient collision, called "strong collision," was an integral part of Rice, Rampsberger, Hinshelwood, and Kassel statistical (RRK) theory as it was part of the early Marcus RRKM theory. However, strong collision models proved an oversimplification of a much more complicated energy transfer process.

Careful experiments in the late fifties and in the sixties especially by Rabinovitch and co-workers¹ indicated that not all colliders are strong. Instead, it was realized that many colliders transfer only small amounts of energy per collision; that is to say, the collisions are inefficient in transferring energy, i.e., they are weak collisions. One of the aspects of weak colliders is their inability to pump molecules efficiently

up the energy ladder. As a consequence, there is a depletion of populations in levels just below the threshold energy for reaction, E_0 .

Lately, a new type of collision was discovered in which an inordinate amount of energy is transferred in a single binary collision. These collisions, called supercollisions, which were found experimentally^{2–5} and in model calculations,^{6–11} transfer as much as 3000 cm^{-1} in a single collision between an Ar atom and an excited toluene molecule^{12,13} or as much as $10\,000\text{ cm}^{-1}$ in a collision between an excited CS_2 and a cold CO.⁷ There seems to be a probability of 1 in a 800 for a 3000 cm^{-1} transfer to occur.^{12,13} These supercollisions, by virtue of the large value of ΔE which is transferred in a single collision, effect the value of the rate coefficient, collisional efficiency and average energy transferred per collision $\langle \Delta E \rangle$ in a very prominent way. Less than one supercollision SC of $10\,000\text{ cm}^{-1}$ in a 1000 collisions will change the value of the rate coefficient by a factor of 9 in the low pressure region. Less than five SC of the same magnitude in 1000 collisions will change the value of the rate coefficient by a factor of 20.⁹ Similar effects were observed for the collisional efficiency and the values of $\langle \Delta E \rangle$.⁹

In the last few years, quasiclassical trajectory calculations on intermolecular energy transfer were performed on a variety of systems.^{12–23} Using modern computational facilities, it became possible to perform large scale computations which are amenable to statistical interpretations. In one such series of studies on Ar–toluene collisions, it was possible to obtain the temporal¹² and spatial¹³ distributions of energy

transferring collisions. It was found that about 64% of the collisions, at the value of the maximum impact parameter used, are elastic and do not contribute to the energy transfer process. The remaining inelastic collisions exchange energy in, on the average, short collision duration, 680 fs and 230 fs at 300 K and 1500 K, respectively. There is however a distribution of collisional lifetimes which spans more than 500 fs. The average minimal distance of approach of the Ar atom to the nearest atom in the molecule in energy transferring collisions is 0.3 nm and practically independent of collision duration or temperature.¹³ There is, however, a distribution of distances which spans about 0.12 nm, a large value in molecular terms.

In the following we probe the collisional mechanism by singling out certain traits of a collision and exploring it on a *statistical* basis. Specifically, we explore the relative velocity of the Ar atom as it approaches the center of mass of the toluene molecule to find whether a collision is repulsive or long lived and if it is long lived does it stay in one location in the molecule or explores all or part of its molecular space. We do so by looking at a statistical ensemble of collision trajectories. Taking cognizance of the fact that analysis of single trajectories can lead to wrong conclusions in as much as some of them can be nonrepresentative, esoteric ones, we have developed a method which enables us to look at a large statistical sample of trajectories and draw conclusions which are based on statistical sampling. This is discussed in the next section.

II. THEORY

The present work follows the calculational method used in Ref. 12 and discussed in Ref. 23. Briefly, the equations of motion were integrated using a public domain program Venus.²⁴ The intermolecular potential was a pairwise Lennard-Jones potential,

$$V_{ij} = A_{ij} r_{ij}^{-12} - B_{ij} r_{ij}^{-6}. \quad (1)$$

The parameters in Eq. (1) are those used previously¹² namely, for the H \cdots Ar interactions $A_{ij} = 9.419\,65 \times 10^{-7}$ kJ mol $^{-1}$ nm (Ref. 12) and $B_{ij} = 1.3651 \times 10^{-3}$ kJ mol $^{-1}$ nm.⁶ For the C \cdots Ar interactions $A_{ij} = 4.982\,148 \times 10^{-6}$ kJ mol $^{-1}$ nm (Ref. 12) and $B_{ij} = 4.9369 \times 10^{-3}$ kJ mol $^{-1}$ nm.⁶ These correspond to (atom–atom) van der Waals radii of 0.335 nm and 0.355 nm for H \cdots Ar and C \cdots Ar, respectively, and atom–atom well depths of 42 and 104 cm $^{-1}$, respectively.

The intramolecular potential includes the contributions of the stretching, bending, wagging, and torsion normal modes

$$V = \sum V_{\text{stretch}} + \sum V_{\text{bend}} + \sum V_{\text{wag}} + \sum V_{\text{torsion}} \quad (2)$$

obtained from Draeger's modified valence force field calculations of force constants given in Ref. 23. They reproduce successfully the experimental normal mode frequencies.

The initial translational and rotational energies were chosen from the appropriate thermal energy distributions at 300 K. The initial impact parameter was chosen randomly be-

tween 0 and its maximum value b_m . The initial orientation of the molecule–bath colliding pair was randomly chosen by rotation through Euler's angles. The internal energy was 30 000 cm $^{-1}$ + the equivalent zero point energy of 27 924 cm $^{-1}$ for a total of 57 924 cm $^{-1}$.

As will be shown later, it is very hard to determine the exact instants at which a collision starts and when it ends. A simple visual observation of a trajectory often proves frustratingly futile in singling out the two end points. Therefore, we have developed a method which performs the end-points detection process in a systematic way. It does so by defining the instances at which a collision is initiated and terminated as the times at which the internal energy is changed by a quantity ϵ during a time interval τ . These initial and final moments are determined by the forward and backward sensing (FOBS) method.¹² In this method each trajectory is scanned forward until a change ϵ is observed in the internal energy of the hot molecule and the time is noted. Then, the trajectory is scanned backward from end to start until again a change ϵ is detected and the time noted again. These two times bracket the collisional event. This method is preferable to detecting changes in the translational energy e.g. relative velocity since the change in the internal energy is due not only to the change in the translational energy but also to the contribution of the intermolecular potential energy. Looking for minimum intermolecular distance as a criterion for the start and end of a collision is problematic. The value of the critical distance of closest approach, the minimal distance, is hard to define and to correlate with the start of the collision.

The value of ϵ used in our calculations was chosen after a careful study in which ϵ was changed systematically and a value chosen such that small variation in ϵ did not change the initial time or duration of the collision. For each trajectory the change in energy was noted as well as its duration as determined by FOBS.

The value of the maximum impact parameter b_m was determined separately.¹² A value of 1.1 nm was used in the present calculations. A systematic study of post collision distances between Ar and the closest atom of toluene has shown that for distances larger than 0.8 nm, no changes in the values of the integral of $\langle \Delta E \rangle$ were observed, therefore, this value was taken as the terminal distance for all trajectories and the end point from which the back sensing of FOBS was initiated. After studying the convergence of $\langle \Delta E \rangle$ as a function of the number of trajectories, a number of 10 000 was chosen.

For each trajectory, the duration of the collision was determined by FOBS and binned according to its lifetime. The bins' widths were 20 fs and 100 fs. That is to say for a given bin width, all collisions with lifetimes up to 20 fs were allocated to the first bin, those with collision lifetimes between 20 and 40 fs were allocated to the second bin and so on. This way, the distribution of collision durations could be obtained.¹² The size of the bins was checked in a systematic way and it was found that below 20 fs the number of trajectories in a bin was too small. In the present work we are interested in the incremental average velocity, $\langle v(t) \rangle$, of the Ar atom relative to the center of mass (CM) of the toluene

molecule as a function of time, t , during the collision. To obtain that, the distance of the Ar atom from the center of mass of the molecule in each trajectory was differentiated with respect to time. This was done for each trajectory j at a given bin. The center of mass velocities at each bin thus obtained, were then averaged at 20 fs intervals. Thus, an average velocity as a function of time is obtained,

$$\langle v(t, \Delta t) \rangle = \sum_{j=1}^n v(t, \Delta t, j) / n, \quad (3)$$

where n is the number of trajectories in the bin.

Equation (3) gives, then, the *average* center of mass velocities as a function of time from the beginning of the collision, $t=0$, to its end $t=\Delta t$ where Δt is the collision duration belonging to a given bin.

III. RESULTS AND DISCUSSION

The underlying philosophy of the present and previous work^{12,13} is to use statistical methods based on many trajectories instead of using single trajectories to draw conclusions about the nature and mechanism of collisions. Among the 10 000 trajectories used in the present study it is always possible to find short lived or long lived trajectories or for that matter, any exotic trajectory one can think of. It is what the bulk of the *energy transferring* trajectories do which determine the nature of the collision process.

Figure 1 demonstrates the method by which trajectories were evaluated. One line in (a) shows the energy before, during and after the collision as function of time. It is a down collision since the final value of the internal energy of the toluene molecule is lower than the initial one. The vertical dotted lines indicate the initial and final points at which a change in internal energy ϵ took place. The time elapsed between these points is the *collision duration*. The second line in (a) is the distance of the Ar atom from the CM of the toluene molecule. As can be seen, the distance during the collision event does not change much, unlike the distance before and after the collision. Differentiation of this line with respect to time yields the relative CM velocity $v(t)$ depicted in (b). Negative values of $v(t)$ indicate that the Ar approaches the CM of the toluene molecule while positive values indicate that it recedes from it. In this particular trajectory the collision lasts 600 fs and starts at a distance of 0.464 nm from the CM of toluene. The Ar comes almost to a complete rest after 200 fs at a distance of 0.428 nm from the CM of toluene. It then accelerates again toward the CM reaching the minimum distance of 0.394 nm after an elapsed time of 500 fs. It then takes off and recedes at great speed from the collision site.

What can be learned from this trajectory and what conclusions can not be drawn from it? We have examined the location of the Ar atom with respect to the nearest atom to it in the toluene molecule as a function of time at 20 fs intervals. We find that the Ar jumps from one location to another during the collision event. This behavior can be explained in the following way. The Ar–toluene potential surface is a multivalley one.^{25,26} Some of the minima are on the periph-

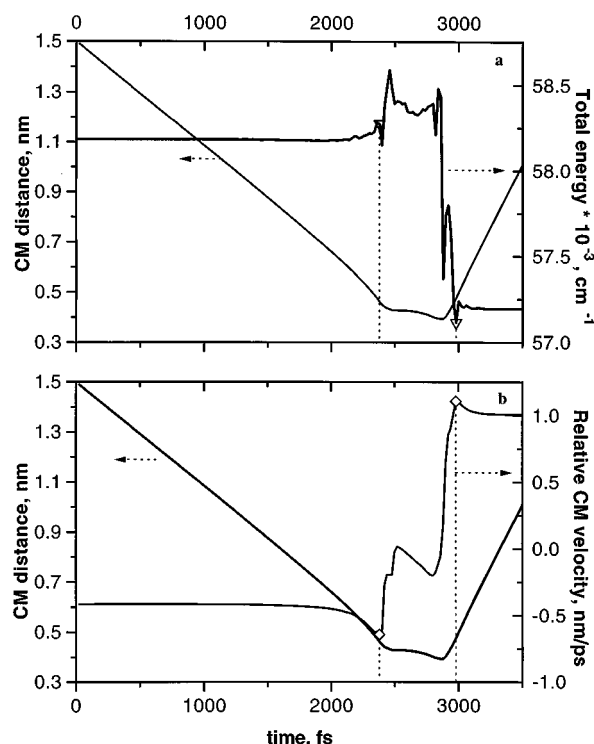


FIG. 1. (a) A trajectory showing the internal energy and the distance between the Ar atom and the center of mass of the toluene molecule vs time. The vertical lines indicate the beginning and end of the collision determined by FOBS. (b) The relative velocity and distance between the Ar atom and the center of mass of the toluene molecule.

eral of the ring above the carbon atoms or between them with the deepest one being in the center of the ring. As the Ar approaches the toluene molecule, it gets hung-up at the peripheral minima, jumping from one minimum to another. This occurs at a rather large distance of 0.428 nm. It then approaches the CM and attains a minimum distance of 0.394 nm. So, the Ar is caught in a deep, local minimum. This distance is larger than the 0.36 nm van der Waals distance.^{23,26} During the whole event, the CM velocity does not remain constant but changes with time and location of the Ar relative to the CM.

How does the Ar acquire its additional kinetic energy (note that the value of the incoming velocity is smaller than the outgoing one)? For reasons which will become apparent shortly, we will not, yet, be specific about this point. We can, however, point out that quantum mechanical calculations on the Ar–benzene system indicate that the out-of-plane ring vibrations of benzene are responsible for the energy transfer process.²⁷ Similarly, in a classical sense, it can be imagined that the Ar is “kicked” by an out-of-plane vibration or an overall rotation. The details of the trajectory all point in this direction. In-plane motion where the atom is hit by a head on collision is possible but obviously very rare.

A. Types of collisions

Correct and appealing as the above analysis is for a single trajectory, it has its pitfalls when general conclusions are to be drawn. For example, among the 10 000 trajectories

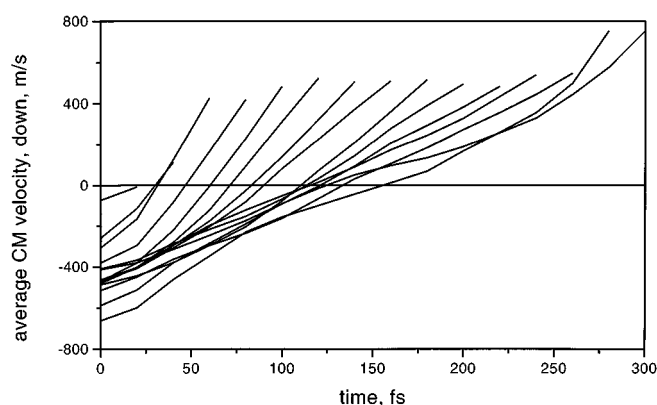


FIG. 2. Average center of mass velocities for down collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations of up to 300 fs are reported. 10 000 Ar-toluene trajectories and collision durations of 20 fs bins were used.

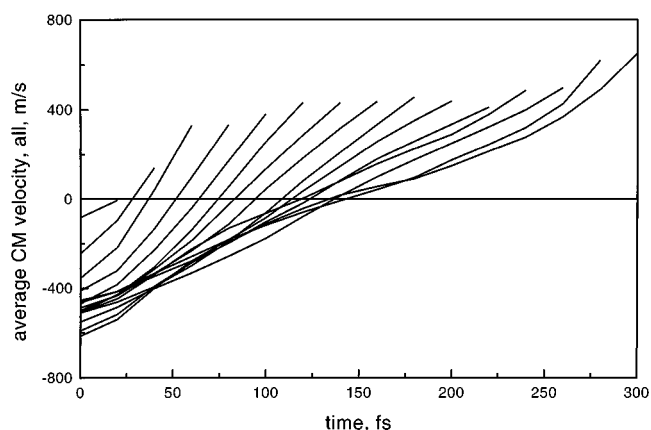


FIG. 4. Average center of mass velocities for all collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations of up to 300 fs are reported. 10 000 Ar-toluene trajectories and collision durations of 20 fs bins were used.

which were run, some were long lived and some were short lived, some had a 0 impact parameter and were in the plane of the molecule and some had 0 impact parameter and were perpendicular to it and so on. To draw a general conclusion it is important to take in consideration *all* trajectories and derive conclusions based on statistical considerations. Figures 2–7 show what happened when such an approach is taken.

Figures 2–7 show the average velocity obtained by averaging, at 20 fs intervals, all the velocities of all the inelastic trajectories in a given collision duration bin. The temporal bins are 0–20 fs, 20–40 fs, and so on at 20 fs intervals. The 20–40 fs bin represents all collisions of duration between 20 and 40 fs.

Of the total number of trajectories 64% are elastic and do not contribute at all to the energy transfer process. 31.6% are energy transferring inelastic collisions with duration of up to 1000 fs. These collisions contribute the bulk of the energy transferred.^{12,13} The remaining 4.4% of the collisions

have longer lifetimes than 1000 fs and contribute only 4 cm^{-1} , which is less than 3%, to the value of $\langle \Delta E \rangle_{\text{all}}$. This group was ignored as a matter of convenience. The various values of the average energy transferred were grouped into 100 fs bins and their value in each bin of a given collision duration are given in Table I.

Observing the values of $\langle v(t) \rangle$ as function of t in Figs. 2–7, a distinct pattern is observed. Up to collision duration of 300 fs the collisions can be termed impulsive, the atom flies in and out without lingering around the molecule at all. These collisions also comprise 62% of all energy transferring collisions and contribute 52% of all the energy transferred $\langle \Delta E \rangle_{\text{all}}$. It is advisable to scan each figure in a general way in order to obtain a overall behavior pattern. The lines are practically straight and simply cross the $\langle v(t) \rangle = 0$ without any change in slope. The whole sequence of events can be

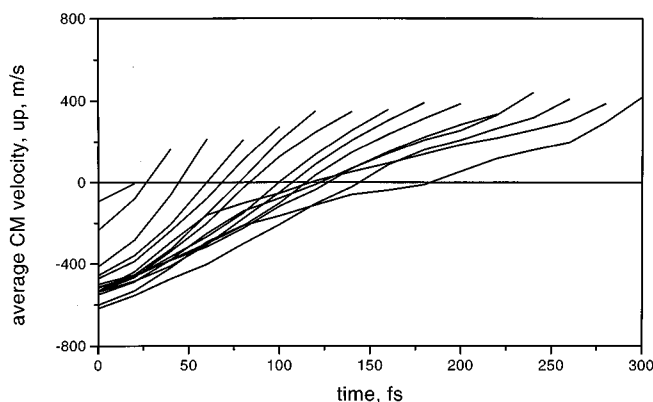


FIG. 3. Average center of mass velocities for up collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations of up to 300 fs are reported. 10 000 Ar-toluene trajectories and collision durations of 20 fs bins were used.

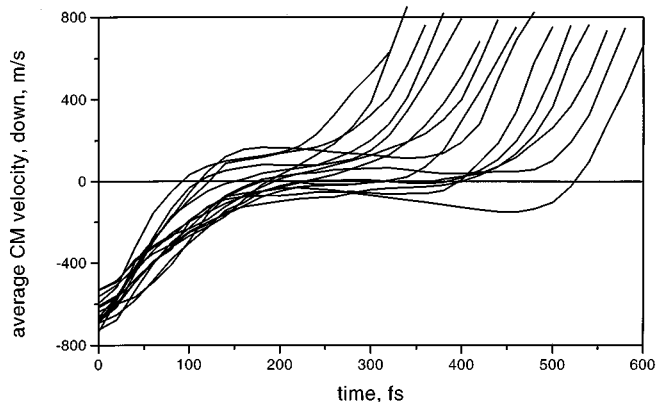


FIG. 5. Average center of mass velocities for down collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations from 300 fs to 600 fs are reported. 10 000 Ar-toluene trajectories and collision durations of 20 fs bins were used.

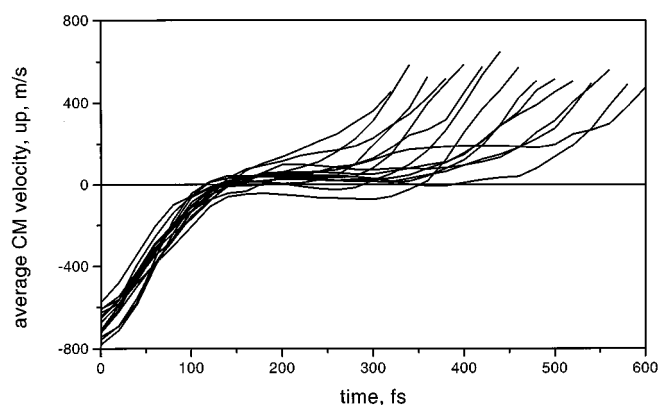


FIG. 6. Average center of mass velocities for up collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations from 300 fs to 600 fs are reported. 10 000 Ar–toluene trajectories and collision durations of 20 fs bins were used.

described as follows. The atom approaches the CM at constant speed. At the beginning of the collision it begins to decelerate at a constant deceleration until it arrives at the minimal distance from the center of mass. Then it accelerates at constant acceleration until the end of the collision.

Figures 5–7 show that in collisions longer than 300 fs the atom slows down and then hovers over the molecule. It never totally comes to rest with respect to the CM but it can obtain almost a constant, low velocity with respect to it. Following a residence period of varying length, depending on the collision duration, it flies away. Figures 5–7 show in greater detail the dramatic change of behavior of this type of collisions from impulsive collisions. Between 300 and 600 fs the Ar slows down lingers a while then takes off again. The rate of deceleration does not vary a great deal from bin to bin. The residence time over the molecule, however, varies a great deal spanning the whole range from few fs to over 300 fs. What is most fascinating is that the acceleration seems to be independent of the residence time and is almost identical for all collisions. This points to the fact that the same mechanism holds for all collisions of this type. The atom is “kicked out” by a fast repulsive process independent of how long it spent at the surface of the molecule.

When the information which can be obtained from a single trajectory as in Fig. 1 is compared with that obtained from averaged behavior as in Figs. 2–7 it is clear that in the latter case some detailed mechanistic information is lost. However, the information which is obtained is much more robust and reliable. In the former case, a single trajectory behavior can be totally uncharacteristic and can lead to erroneous conclusions.

During the last four decades many models and expressions to calculate $\langle \Delta E \rangle$ were proposed.^{28–36} This led to a cumulative confusion where terms such as long lived or short lived collisions were used without quantitative criteria. Based on the above analysis, four types of inelastic collisions appear to exist. We next define their properties.

1. Impulsive (direct) collisions

These are collisions which last less than 300 fs. As Figs. 2–4 show, they approach the CM of the molecule at constant deceleration and depart with constant acceleration without lingering at all at the molecular surface. The range of vibrational periods covered by the impulsive collisions corresponds to molecular vibrations in the range 100–330 cm^{-1} . These values are (barely) within the range of the lowest lying out-of-plane mode [400 cm^{-1} (Ref. 23)] and within the C–C bends [340 and 220 cm^{-1} (Ref. 23)]. It is therefore possible for the atom to be “kicked” in a single vibration. It is also clear that it will be incorrect to assume that the velocity of the atom is simply twice the van der Waals radius divided by the collision duration. This leads to velocities which are an order of magnitude larger than those observed in the present work. As indicated above, impulsive collisions make up the majority of the inelastic collisions. 62% of all inelastic collisions are impulsive and they transfer 52% of the energy.

2. Chattering collisions

These collisions last longer than impulsive collisions. The bath atom moves at a constant velocity around the substrate molecule without departing from it. However, these collisions are too short to allow a complete intramolecular energy redistribution (IVR) to take place during the collision lifetime. We propose that collisions with lifetimes which are bracketed between the lifetimes of direct collisions and intramolecular vibrational redistribution (IVR) lifetimes be called chattering collisions. A chattering collision does not mean that the atom is located in one place relative to the CM of the molecule and exercises a vibrational motion. Rather, a detailed analysis of single trajectories indicate that it hops from one site to another sampling part of the minima in the atom–molecule potential surface.

Chattering collisions comprise the second largest group of collisions after direct collisions. Since IVR times have a large range of values it is hard to pinpoint their exact upper

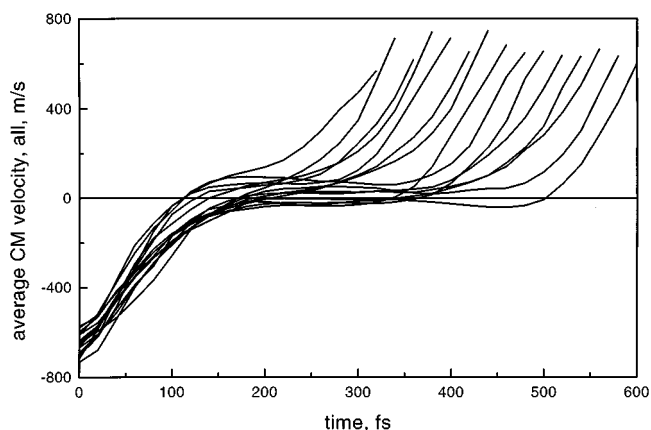


FIG. 7. Average center of mass velocities for all collisions as a function of time from the beginning to the end of the collision as determined by FOBS. The end point of each line indicates the collision duration. Collision durations from 300 fs to 600 fs are reported. 10 000 Ar–toluene trajectories and collision durations of 20 fs bins were used.

TABLE I. Number of trajectories and average energy transferred in all, up and down collisions as a function of the bin number and the collision duration for bin size of 100 fs.

Bin (i)	Time (fs)	N_{all}	N_d	N_{up}	$\langle \Delta E_i \rangle_{\text{all}}$ (cm ⁻¹)	$\langle \Delta E_i \rangle_d$ (cm ⁻¹)	$\langle \Delta E_i \rangle_{\text{up}}$ (cm ⁻¹)
0	...	6408	3302	3103	1.06	-17.36	20.77
1	100	762	400	360	-26.30	-100.38	52.93
2	200	1178	590	588	-20.42	-125.24	91.69
3	300	301	168	133	-11.14	-40.77	20.56
4	400	210	125	85	-15.44	-47.36	18.70
5	500	225	142	83	-16.14	-47.49	17.38
6	600	209	119	90	-18.56	-53.53	18.84
7	700	119	72	47	-6.11	-19.19	7.88
8	800	80	39	41	-1.69	-9.25	6.39
9	900	53	22	31	-1.52	-7.85	5.25
10	1000	32	10	22	0.90	-1.24	3.19

temporal limit. IVR lifetimes in large polyatomic molecules are around 500 fs (Ref. 37) while in a cluster they can be much longer due to the mismatch between the transition modes of the Ar-toluene and the normal modes of the molecule. Hence, it is hard to determine exactly the absolute value, percentagewise, of the chattering collision contribution to the total energy transfer. To judge from the values in Table I, it is no less than 30% and might be even more.

3. Complex-forming collisions

There are two types of complex forming collisions. To type I belong collisions with lifetimes longer than molecular IVR lifetimes. In such a complex, energy is distributed statistically among all the molecular modes but not in the transition modes of the complex. Statistical theories can not be applied to calculate the unimolecular rate coefficient of the complex. The number of such collisions is very small. To type II belong collisions with lifetimes longer than the IVR times of the complex. RRKM theory can be used to calculate rate coefficients for the dissociation of the complex and the kinetic energy release of the fragments. Our results show that the number of these collisions is very small and they hardly contribute to the energy transfer process. This fact was known before from analysis of values of $\langle \Delta E \rangle$ calculated by using statistical models which, inevitably, were much too large compared with experimental results.²⁸ Our results indicate, given that IVR lifetimes are not known precisely, that both types comprise about 4% of all collisions and contribute ~3% of all the energy transferred. Thus, for atom-molecule collisions they can safely be ignored. Similar conclusion was obtained for trajectory calculations of SF₆ relaxation.¹⁹

4. Supercollisions

These are collisions which transfer an inordinate amount of energy in a single event.²⁻¹¹ In the present study we have found that, at 300 K, one collision in 800 transferred ~3000 cm⁻¹. This number is about 7 times the average energy transferred in a down or an up collision. The effect of supercollision on chemical reaction is significant.⁹ One 10 000 cm⁻¹ in 1000 weak collisions of 300 cm⁻¹ will increase the value of the rate coefficient ninefold. In the case of a weak collider

in the low pressure regime supercollisions provide a vehicle by which very energetic collisions transfer a molecule from low lying energy levels directly over the threshold. Ladder climbing by small steps is a very inefficient process in as much as down collisions contribute as much as up collision to the energy transfer process making the overall-up pumping process very slow.

Similar supercollision mechanisms might be operational in solutions. Wilson *et al.*^{35,36} have studied the bimolecular reaction Cl+Cl₂→Cl₂+Cl in liquid Ar as solvent. They found that the excitation of the reactants occurs not in a smooth stepwise process but in few discreet steps which involve supercollision-type events. They have identified in their molecular dynamics calculations four steps which lead to reaction. (a) High translational energy is acquired by few solvent atoms. (b) Hard solvent-reactant collisions producing high potential energy spikes. (c) The potential energy is transformed into translational energy of the reactants. (d) The translational energy of the reactants is converted to potential energy when the barrier is surmounted. This is clearly a mechanism reminiscence of supercollisions in the gas phase.

The mechanistic reasons for the existence of supercollisions are only beginning to be known.³⁸ The problem is that a large statistical sample must be collected before any definite conclusion can be drawn. At the rate of production of one supercollision in 800 collisions a very large number of trajectories must be run, a resource and time consuming process. The available data point out that a prerequisite for a supercollision to occur is that the incoming atom must be in phase with a wide amplitude motion, an out-of-plane vibration or an overall rotation.³⁸ This rare requirement makes supercollisions rare.

B. Comparison with existing energy transfer models

How do existing energy transfer models agree with the above findings? The biased random walk (BRW) model³² assumes that the collision is a chattering collision or a long-lived complex forming collision. It is assumed that during the collision duration energy diffuses in the excited polyatomic molecule. The value of the average energy transferred in a collision is given by the expression $\langle \Delta E \rangle = Dt_c$, where

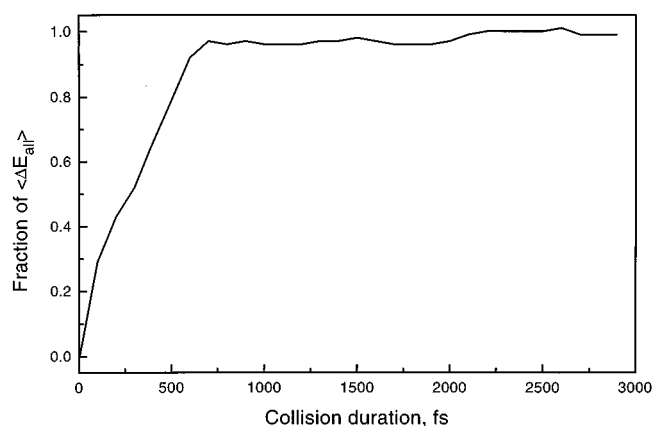


FIG. 8. The dependence of the integrated value of $\langle \Delta E \rangle$ on collision duration for all 10 000 trajectories.

D is the energy diffusion and t_c is the collision duration. The longer the collision duration the more energy is transferred on the average from the hot molecule to the cold atom. This is not borne out by our trajectory results¹² which show that there is a distribution in lifetimes which falls to 0 at long collision durations. If one plots the integrated value of $\langle \Delta E \rangle$ vs time, Fig. 8, a saturation curve is obtained. Time in this figure is measured from the onset of the experiment and it encompasses all collision durations up to a final time t_f .

Dashevskaya *et al.*^{33,34} have developed the sequential direct encounter (SDE) model in which energy is removed by a sequence of impulsive-direct encounters of the atom with the excited molecule in what might look like a chattering collision. Each impulsive encounter exchanges energy proportional to $\exp(-\Omega^*\tau)$, where Ω is the low molecular frequency and τ is the encounter duration. The collision event, which is composed of sequential encounters, has a lifetime t_c which is temperature dependent. The value of the average energy transferred per collision is given by

$$\langle \Delta E \rangle = [zt_c / (\lambda zt_c + 1)](E - E_{\text{eq}}). \quad (4)$$

In this model $\langle \Delta E \rangle$ does not increase linearly with t_c but it reaches a finite value in agreement with the present trajectory calculation results. γ , z , and E_{eq} are complicated constants given in Refs. 33 and 34.

IV. CONCLUSIONS

Quasiclassical trajectory calculations were performed on the Ar–toluene collision pair. The trajectories were binned according to their collision duration. The velocity of the Ar atom relative to the center of mass of the toluene molecule was evaluated by differentiating the distance of the Ar atom from the center of mass of the toluene with respect to time. The velocities at each bin were averaged to give the average velocity of the Ar atom with respect to the center of mass of the toluene as function of time. The collisions were divided into four types.

(a) Impulsive collisions, the Ar atom comes in and goes

out without lingering around the molecule. They last less than 300 fs and comprise 62% of all inelastic collisions.

- (b) Chattering collisions, they are less abundant but still common, $\sim 30\%$. The Ar atom hops from minimum to minimum on the multi minima potential hypersurface. The durations of these collisions are longer than 300 fs but shorter than IVR times and thus are not amenable to statistical theories.
- (c) Complex forming collisions. Their number is very small and they hardly contribute to the energy transfer process.
- (d) Supercollisions. One in 800 collisions was found to be a supercollision which transferred $\sim 3000 \text{ cm}^{-1}$ in a single collisional event.

Recent energy transfer models were evaluated and compared with the results of the present study. It is shown that the value of the average energy transferred in a collision remains practically constant at collision durations above 700 fs. Thus models that predict linear dependence of the average energy on the collision duration must be modified. It is suggested that supercollisions in gas phase and in solutions, which are characterized by transferring large quantities of energy in very short times, contribute in a major way to the rate of chemical reaction.

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¹D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.* **77**, 369 (1977).

²A. Pashutzky and I. Oref, *J. Phys. Chem.* **92**, 178 (1980).

³S. Hassoon, I. Oref, and C. Steel, *J. Chem. Phys.* **89**, 1743 (1988).

⁴I. M. Margulis, S. S. Sapers, C. Steel, and I. Oref, *J. Chem. Phys.* **90**, 923 (1989).

⁵A. S. Mullin, J. Park, J. Z. Chou, G. W. Flynn, and R. E. Weston, *Chem. Phys.* **53**, 175 (1993).

⁶D. L. Clarke, K. G. Thompson, and R. G. Gilbert, *Chem. Phys. Lett.* **182**, 357 (1991).

⁷G. Lendvay and G. C. Schatz, *J. Phys. Chem.* **94**, 8864 (1990).

⁸I. Oref, in *Vibrational Energy Transfer Involving Small and Large Molecules*, edited by J. R. Barker (JAI, New York, 1995), Vol. 2.

⁹V. Bernshtein and I. Oref, *J. Phys. Chem.* **97**, 12 811 (1993).

¹⁰V. Bernshtein and I. Oref, *J. Phys. Chem.* **98**, 3782 (1994).

¹¹I. Oref, *Chem. Phys.* **187**, 163 (1994).

¹²V. Bernshtein, K. F. Lim, and I. Oref, *J. Phys. Chem.* **99**, 4531 (1995).

¹³V. Bernshtein and I. Oref, *Chem. Phys. Lett.* **233**, 173 (1995).

¹⁴N. Date, W. L. Hase, and R. G. Gilbert, *J. Phys. Chem.* **88**, 5135 (1984).

¹⁵N. J. Brown and J. A. Miller, *J. Chem. Phys.* **80**, 5568 (1984).

¹⁶M. Bruehl and G. C. Schatz, *J. Chem. Phys.* **89**, 770 (1988).

¹⁷M. Bruehl and G. C. Schatz, *J. Phys. Chem.* **92**, 7223 (1988).

¹⁸G. Lendvay and G. C. Schatz, *J. Chem. Phys.* **96**, 4356 (1992).

¹⁹G. Lendvay and G. C. Schatz, *J. Chem. Phys.* **98**, 1034 (1993).

- ²⁰G. Lendvay and G. C. Schatz, *J. Phys. Chem.* **94**, 8864 (1990); **96**, 3752 (1992).
- ²¹K. F. Lim and R. C. Gilbert, *J. Phys. Chem.* **94**, 72 (1990); **94**, 77 (1990).
- ²²D. L. Clarke, I. Oref, R. G. Gilbert, and K. F. Lim, *J. Chem. Phys.* **96**, 5983 (1992).
- ²³K. F. Lim, *J. Chem. Phys.* **100**, 7385 (1994); **101**, 8756 (1994).
- ²⁴Venus, Quantum Chemistry Program Exchange by W. L. Hase, R. J. Duchovic, X. Hu, K. F. Lim, D. H. Lu, G. Pesherbe, K. N. Swamy, S. R. Vande-Linde, and R. J. Rolf, Quantum Chemistry Program. Exchange Bull.
- ²⁵P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Chem. Phys.* **95**, 391 (1991).
- ²⁶P. Hobza, H. L. Selzle, and E. W. Schlag, *Chem. Rev.* **94**, 1767 (1994).
- ²⁷D. C. Clary (private communication).
- ²⁸I. Oref and D. C. Tardy, *Chem. Rev.* **90**, 1407 (1990).
- ²⁹R. G. Gilbert, *Int. Rev. Phys. Chem.* **10**, 319 (1991).
- ³⁰H. Hippler and J. Troe, in *Bimolecular Reactions*, edited by J. E. Baggott and M. N. R. Ashfold (The Chemical Society, London, 1989).
- ³¹D. C. Tardy, *J. Chem. Phys.* **99**, 963 (1993).
- ³²K. F. Lim and R. G. Gilbert, *J. Chem. Phys.* **84**, 6129 (1986); **92**, 1819 (1990); R. G. Gilbert and I. Oref, *J. Phys. Chem.* **95**, 5007 (1991).
- ³³E. Dashevskaya, E. E. Nikitin, and I. Oref, *J. Phys. Chem.* **97**, 9397 (1993).
- ³⁴E. Dashevskaya, E. E. Nikitin, and I. Oref, *J. Phys. Chem.* **99**, 10797 (1995).
- ³⁵K. R. Wilson and R. D. Levine, *Chem. Phys. Lett.* **152**, 435 (1988).
- ³⁶I. Benjamin, B. J. Gertner, N. J. Tang, and K. R. Wilson, *J. Am. Chem. Soc.* **112**, 524 (1990).
- ³⁷I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.* **12**, 166 (1979).
- ³⁸D. C. Clary, R. G. Gilbert, and I. Oref, *Faraday Discussions* No. 102 (1995) (in press).