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How a Collision Complex forgets its Origin: H_3^+

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By means of classical trajectory calculations we investigate how a collision complex 'forgets' its origin. Our specific example is the collision of H^+ with H_2 , and isotopic variants of this reaction. The process of loosing the correlation between input and output parameters can be considered as a generalization of intramolecular vibrational relaxation. Indicators for the time to 'forget', which we call the induction time, are derived from average intramolecular distances during the collision, and from angular distributions and branching ratios after the collision. Induction times are determined as a function of translational, vibrational and rotational initial energy supply, and, in some cases, total angular momentum and masses.

The distinction between direct and complex collisions is by now well established:¹ a complex collision is one in which the system has 'forgotten' from which atoms and from which states it was prepared, from which direction its constituents came, and how the total energy was deposited into the system, while the outcome of a direct collision depends strongly on these factors. However, these concepts are limiting ones, quantitatively there is a continuum of possibilities between them, which is sometimes interpolated by the concept of the 'osculating complex'.² The time to 'forget', *i.e.* the relaxation time for correlations between incoming and outgoing parameters of the collision, may be different for different properties. It is, therefore, worthwhile to monitor the development of several such properties as a function of time. Moreover, some of them can also be defined if there is no collision to start with, *i.e.* if the system decays unimolecularly and was not prepared by chemical activation, but, *e.g.* by laser excitation. So our results are, in part, very similar to a study of intramolecular vibrational redistribution (IVR).

In view of the unfeasibility of extensive quantum scattering calculations for realistic molecular models, we use quasi-classical trajectories in this work. Apart, perhaps, from systems with very few quantum states, one does not expect that the properties which we monitor are very sensitive to quantum effects. The varied input parameters were translational, vibrational and rotational initial energies, and, in some cases, total angular momentum and masses. To be specific, our calculations were performed for H_3^+ , *i.e.* the scattering process

(with distinguishable protons), whose potential-energy surface is well known. Note, however, that in classical mechanics scaling is possible, and allows one to write any time-like physical magnitude of our system in the form

$$\tau = \sqrt{\left(\frac{Mr_0^2}{D}\right)} f\left(\frac{E_i}{D}, \frac{J}{\sqrt{(Mr_0^2 D)}}, \frac{m_j}{M}, c_k\right) \quad (1)$$

where E_i are the different initial energy contributions (translational, vibrational, rotational), D the well depth, J the total angular momentum, m_j the masses, M the total mass, r_0 the linear size of the potential well, the c_k dimensionless potential shape parameters, and $f(\)$ some function of the given arguments. In other words, H_3^+ and Ar_3 , which both have a potential well with symmetry D_{3h} , behave classically alike, if all energies, J , M and r_0 are properly scaled. So, the calculation for one single molecule should at least give an indication for the behaviour of a whole class of similar molecules.

Calculational Details

Scattering trajectories were started in batches of 10^3 to 10^4 in the standard way.³ In most cases the collision energy E_{tr} , and the diatom's angular momentum, j , and vibrational quantum number, v , were prescribed. In most runs the impact parameter, b , was randomly selected with weight bdb . In this case one obtains an averaged result which is weighted with $P_c(J)$, the complex formation probability as a function of J . Our integrating routine is of the Gear type,⁴ note that we adjusted its accuracy parameter such that our trajectories were back-integrable for the times needed (generally 500 fs).

As before,³ we introduce the number, n_{MW} , of 'minimum exchanges' as a mass-independent measure of the duration of a collision. n_{MW} is defined as the number of changes in the identity of the smallest of the internuclear distances R_i ($i = 1-3$). Somewhat simplifying, one can think of n_{MW} as counting the vibrations performed by the systems. We define the lifetime of a complex as the interval from its first minimum exchange to the last one. This avoids the trivial but strong influence of the collision energy on the duration of the collision, which comes from the intermolecular approach if the time is set as zero at the start of the trajectory. The average time interval between two minimum exchanges is nearly constant after the first two or three exchanges; it is slightly dependent on total energy, and scales with total mass M to within 5%. For H_3^+ one minimum exchange is equivalent to 6–8 fs increasing slightly with total energy.

An accurate potential-energy surface of H_3^+ is well known.⁵ However, for our purposes a simpler surface suffices, so we use either the DIM potential,⁶ or a still simpler one made from three internuclear Morse potentials

$$V(R_1, R_2, R_3) = \sum_i^3 V_i(R_i) \\ V_i(R_i) = D\{\exp[2\beta(R_0 - R_i)] - 2\exp[\beta(R_0 - R_i)]\} \quad (2)$$

where $D = 3.223 \text{ eV}^\dagger$ is the well depth of a diatomic fragment (the well depth of the triatomic molecule is $2D$), $\beta = 1.5661 \text{ \AA}^{-1}$ the width parameter, and $R_0 = 0.91765 \text{ \AA}$ the equilibrium distance of a pair of nuclei. Note that this potential has only one shape parameter, βR_0 .

Results

Internuclear Distances

The first thing which comes to mind when discussing complex collisions is the angular distribution, which is

[†] 1 eV $\approx 1.60218 \times 10^{-19} \text{ J}$.

Fig. 1 (—) Plot of the ratio $\rho = \max(R_1, R_3)/R_2$ averaged over 1500 trajectories vs. time. $\text{H}^+ + \text{H}_2$, $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV, $J = 40$. (---) Exponential fits showing that τ is 64 ± 15 fs.

expected to be uniform on a sphere if there is no angular momentum constraint.^{1,2} However, we shall see that this distribution is not a good indicator for induction times. So we will start our discussion by investigating magnitudes which are not directly measurable but easily obtained in the simulation: the average internuclear distances during the collision. Specifically, we take the average over 1500 trajectories of the ratio

$$\rho = \max(R_1, R_3)/R_2$$

as a function of t . Here R_2 is the distance between that pair of atoms which originally was the diatom. The calculation was performed using eqn. (2). An example is shown in Fig. 1. The relaxation of ρ and the dephasing of the molecular vibration with respect to time zero, the first minimum exchange (*i.e.* the first hard encounter), is easily seen. After about eight vibrations (100 fs) the dephasing is almost complete. The relaxation of ρ to its asymptotic value, 1, can in this case be well represented by an exponential decay with a time constant τ of about 64 fs.

The observed values are given in Table 1. Their dependence on E and J can be rationalized as follows. For a given E , τ increases with J , almost doubling from an average J to values near J_{max} , the total angular momentum above which complexes are no longer formed (see below). This effect can be understood as due to the centrifugal force, which keeps the nuclei away from each other, and the Coriolis force, which deflects their motion sideways, *i.e.* makes the encounters 'softer'. In contrast, the dependence of τ on E at fixed J is not pronounced, except again when $J_{\text{max}}(E)$ is approached.

Angular Distributions

Let us now look at the classical parameter connected with complex formation, which has played such a big role in the

Table 1 Induction time τ /fs determined from the averaged largest relative internuclear distance

$J/\hbar$	collision energy/eV				
	0.1	0.25	0.5	1.0	1.5
0	$(30 \pm 35)^a$		— ^b	$(10 \pm 27)^a$	
10	— ^b		$(2 \pm 8)^a$	$(4 \pm 14)^a$	
20	7.5 ± 5	10 ± 9	32 ± 21	$(52 \pm 84)^a$	
25	16 ± 5	28 ± 12	25 ± 13	19 ± 19	— ^b
30	— ^c	31 ± 8	35 ± 14	38 ± 23	27 ± 26
35	— ^c	53 ± 12	39 ± 12	37 ± 16	34 ± 21
40	— ^c	— ^c	64 ± 15	44 ± 12	— ^c

^a Non-significant values of τ . ^b Cases where the likelihood function gave no maximum. ^c Combinations of E and J for which no complexes are formed.

discussion of reactive collision experiments since the 1960s:² the angular distribution of scattering products. In normalized form we write it as

$$f(\theta; C_1, C_2) = \frac{1}{\pi} + C_1 \cos \theta + C_2(\cos^2 \theta - \frac{1}{2}) \quad (3)$$

For a 'long-lived complex', C_1 and C_2 should become zero after the induction time. C_1 determines the forward-backward ratio, which is, for in-plane scattering,

$$\frac{P_f}{P_b} = \frac{\frac{1}{2} + C_1}{\frac{1}{2} - C_1} \quad (4)$$

while C_2 determines the ratio of sideways to forward plus backward scattering. Both parameters and their errors were determined as maximum likelihood estimates.^{7,8} In contrast to the previous section, the complex must now decay, before the scattering angle is defined. Ideally, one should compute the C_i for complexes decaying in a short time interval at time t , but the limited statistics forbid this. So we computed the parameters C_i for all complexes decaying after a given time, or rather after a given number of minimum exchanges, as explained above.

Table 2 shows the results, which were computed with the DIM potential.⁶ Unfortunately, in spite of many trajectories started, the yield is meager. Perhaps unexpectedly, forward scattering is suppressed in all cases except for $E_{\text{tot}} = 1.5$ eV (note the sign), if the short trajectories ($n_{\text{MW}} \geq 2$) are included, but the later values of C_1 are compatible with a forward-backward ratio of one. In addition, also in contrast to expectations, sideways scattering, if significant at all, is preferred rather than suppressed.

In order to understand this, one must discuss the rotation periods of the complexes in our samples. Given the rotational constant, B , and total angular momentum quantum number, J , the rotation period is $T = T_1/J$ with $T_1 = h/2B$ (or $1/2cB$, if B is measured in cm^{-1}). T_1 is 600 fs for H_3^+ . Complexes can be formed at a given energy, E , up to an angular momentum $J_{\text{max}}(E)$, which can be computed from the potential, applying the usual Langevin condition. (We use the correct model potential, not the polarizability of H_2 in this calculation.) A good fit for the DIM potential gives $J_{\text{max}} = 54.39E^{0.316}$, resulting in limiting angular momenta from 26 at $E = 0.1$ eV to 62 at $E = 1.5$ eV. This leads to rotation periods T_1 between 23 and 10 fs. However, since we generally consider (in computations as well as in the experiments) a mixture of angular momenta, we must look for the distribution of periods. It is given by the *a priori* weight of J , which is proportional to J , and the energy-dependent complex formation probability $P_c(J)$. Examples of this function have been determined on several occasions.^{3,9-11} A new example is shown in Fig. 2 and three simple model probabilities are in shown in Fig. 3. Their effect can easily be evaluated: The 'ideal' model (a), which, however, is valid only for collision energies below about 0.1 eV (1/50 of the well depth), gives $\langle J \rangle = 2/3J_{\text{max}}$ and $\langle T \rangle = T(J_{\text{max}}/2)$. Model (b), which resembles Fig. 2, and is valid for $E_{\text{tr}} \approx 0.5$ eV, gives $\langle J \rangle = 1/2J_{\text{max}}$ and $\langle T \rangle = T(J_{\text{max}}/3)$, while model (c), valid at about 1.5 eV, gives $\langle J \rangle = 1/6J_{\text{max}}$ and $\langle T \rangle = T(J_{\text{max}}/4.5)$. The increase of J_{max} and the decrease of P_c with E_{tr} largely compensate, and we find an average rotation period of about 45 fs for all our samples. This is equivalent to about five minimum exchanges, and explains why Table 2 shows no sign of an induction time.

Thus, in mixed- J samples the relation between the establishment of forward-backward symmetry of the cross-section and a timescale which indicates complex formation must be discussed very carefully. The complex formations defined as (i) the relaxation of all internal correlations, and (ii) the loss

Table 2 Coefficients of angular distributions of complexes decaying after at least n_{MW} minimum exchanges^a

initial condition	n_{MW}	N	C_1	C_1/σ_1^b	C_2	C_2/σ_2^b
$E_{\text{tot}} = 0.1$	2	61	-0.18	3.5	-0.04	0.4
$E_{\text{tr}} = 0.1$	5	25	-0.04	0.5	-0.06	0.3
$E_v = 0$	8	16	-0.08	0.8	-0.08	0.3
$E_{\text{rot}} = 0$	16	8	-0.18	1.3	-0.08	0.3
$E_{\text{tot}} = 0.25$	2	164	-0.09	2.6	-0.05	0.8
$E_{\text{tr}} = 0.1$	5	97	-0.01	0.3	-0.13	1.4
$E_v = 0.15$	8	79	-0.04	0.9	-0.18	1.8
$E_{\text{rot}} = 0$	16	59	-0.04	0.8	-0.26	2.4
$E_{\text{tot}} = 0.5$	2	728	-0.03	1.6	0.01	0.2
$E_{\text{tr}} = 0.1$	5	556	0.03	1.4	-0.02	0.5
$E_v = 0.4$	8	507	0.03	1.3	-0.01	0.3
$E_{\text{rot}} = 0$	16	385	0.00	0.1	-0.02	0.3
$E_{\text{tot}} = 1.0$	2	1416	-0.08	6.6	-0.03	1.2
$E_{\text{tr}} = 0.1$	5	1055	-0.03	2.2	-0.08	2.9
$E_v = 0.9$	8	910	-0.03	2.4	-0.09	2.8
$E_{\text{rot}} = 0$	16	653	-0.03	2.0	-0.08	2.2
$E_{\text{tot}} = 0.25$	2	320	-0.13	5.5	-0.06	1.3
$E_{\text{tr}} = 0.25$	5	137	-0.03	0.7	-0.09	1.2
$E_v = 0$	8	110	-0.04	0.9	-0.09	1.1
$E_{\text{rot}} = 0$	16	78	-0.04	0.8	-0.18	1.8
$E_{\text{tot}} = 0.5$	2	3729	-0.08	11.1	-0.03	1.8
$E_{\text{tr}} = 0.5$	5	1758	0.01	0.5	-0.05	2.5
$E_v = 0$	8	1521	0.02	1.8	-0.04	1.8
$E_{\text{rot}} = 0$	16	1159	0.01	0.4	-0.04	1.4
$E_{\text{tot}} = 1.0$	2	1063	-0.09	6.7	-0.11	3.8
$E_{\text{tr}} = 1.0$	5	380	-0.04	1.6	-0.12	2.5
$E_v = 0$	8	318	-0.03	1.1	-0.10	1.9
$E_{\text{rot}} = 0$	16	233	-0.04	1.2	-0.05	0.8
$E_{\text{tot}} = 1.5$	2	1463	0.05	5.9	-0.39	19.5
$E_{\text{tr}} = 1.5$	5	403	0.01	0.2	-0.16	3.5
$E_v = 0$	8	318	0.03	1.1	-0.11	2.0
$E_{\text{rot}} = 0$	16	227	-0.00	0.1	-0.08	1.4
$E_{\text{tot}} = 0.5$	2	652	-0.05	2.6	-0.09	2.4
$E_{\text{tr}} = 0.1$	5	522	-0.00	0.2	-0.13	3.2
$E_v = 0$	8	453	0.00	0.2	-0.12	2.7
$E_{\text{rot}} = 0.4$	16	369	0.02	0.8	-0.12	2.4

^a Between 1000 and 10000 trajectories were started with the initial conditions shown, of which N remained for evaluation. ^b The columns C_i/σ_i give the ratio of C_i to its mean square error, only entries ≥ 1 are usually considered significant.

of the correlation between the incoming and outgoing directions are two very different things.

Product Branching

The last parameter which we have investigated is the branching of the decay products into the three possible channels. Again, we consider only trajectories which decayed after a certain number of minimum exchanges. In view of the limited statistics we do not distinguish between the two different reactive channels, but look for the probability that the non-reactive channel 2 is chosen. The DIM potential is used. Fig. 4 shows an example in the form of a histogram. We take a simple exponential *ansatz*

$$P_2(t) = C_1 + C_2 \exp(-t/\tau) \quad (5)$$

and try to determine the three parameters by the maximum likelihood method. Since estimation of three free parameters from our data led to insignificant results, a compromise had to be made.

We first determined the asymptotic branching ratio C_1 assuming $C_2 = 0$. It turned out to be very robust both

Fig. 2 (—) Probability of complex formation, i.e. of making ≥ 8 minimum exchanges. (---) Probability of capture, i.e. > 0 minimum exchanges, vs. impact parameter b . $\text{H}^+ + \text{H}_2$, $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV. b_L is the Langevin capture impact parameter.

Fig. 3 Three model functions for the complex formation probability vs. total angular momentum. For $\text{H}^+ + \text{H}_2$; (a) $E_{\text{tr}} \leq 0.1$ eV, (b) to $E_{\text{tr}} \approx 0.5$ eV, and (c) to $E_{\text{tr}} \approx 1.5$ eV.

against variations of the amount and kind of initial energy, and against variation of the number of minimum exchanges if this number exceeded 30. For masses 1, 1, 1 the average over eight batches of trajectories with different initial conditions was 0.331 ± 0.039 . (It is, however, mass dependent, see below.) We then fixed $C_1 = 1/3$, $C_2 = 2/3$ and determined only τ . The results for eight different initial conditions are shown as case (a) in Table 3. Alternatively, we determined two coefficients assuming only the relation $C_1 + C_2 = 1$. This is case (b) in Table 3; naturally the errors of τ are now greater. Especially in the two cases in which the value of C_2

Fig. 4 Branching ratio P_2 into non-reactive channel vs. time after which decaying complexes are included. $\text{H}^+ + \text{H}_2$, $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV.

Table 3 Induction times derived from the relaxation of the branching ratio P_2 to its asymptotic value [cf. eqn. (5)] for different initial energy supplies^a

energy/eV				$C_2 = 1 - C_1^c$			
E_{tot}	E_{tr}	E_v	E_{rot}	N	$(\tau \pm \sigma_\tau)/\text{fs}^b$	$C_1 \pm \sigma_1$	$(\tau \pm \sigma_\tau)/\text{fs}$
0.10	0.10	0	0	16	$(20 \pm 32)^d$	0.36 ± 0.15	$(15 \pm 39)^d$
0.25	0.25	0	0	112	48 ± 18	0.24 ± 0.07	69 ± 25
0.25	0.10	0.15	0	79	56 ± 21	0.31 ± 0.07	60 ± 28
0.5	0.5	0	0	1521	77 ± 8	0.43 ± 0.02	32 ± 11
0.5	0.1	0.4	0	507	40 ± 8	0.32 ± 0.03	42 ± 10
0.5	0.1	0	0.4	453	44 ± 11	0.36 ± 0.03	34 ± 18
1.0	1.0	0	0	318	$(18 \pm 22)^d$	— ^e	— ^e
1.0	0.1	0.9	0	910	21 ± 6	0.33 ± 0.02	21 ± 7
1.5	1.5	0	0	318	$(14 \pm 15)^d$	0.37 ± 0.03	$(9 \pm 27)^d$

^a The masses are 1, 1, 1. Only trajectories with ≥ 8 minimum exchanges have been included. ^b $C_1 = 1/3$, $C_2 = 2/3$. ^c $C_1 + C_2 = 1$ was assumed.^d Non-significant values. ^e No maximum of likelihood function found.

from fit (b) is very different from the asymptotic value $1/3$, the corresponding τ s must be treated with caution, even if their nominal error is small.

The values are collected in Fig. 5. Two trends can be seen from this figure and Table 3: (i) An increase of the total collision energy decreases the induction time, (ii) at fixed total energy an increase in the fraction of energy supplied as internal energy also decreases τ .

Table 4 shows that the total angular momentum influences the induction time determined here in the same sense as that discussed in the section on internuclear distance.

Isotope Effects

The influence of varying the nuclear masses was determined for the angular distributions and for the branching ratios. Since the former are not very significant, we abstain from showing them. The latter, however, are significant and show interesting trends. Their knowledge is important if one wants to scale our results to other ABC molecules. Table 5 presents first the asymptotic branching for five mass combinations at $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV.

The results are qualitatively as expected from phase space considerations. For a quantitative comparison, one must take into account both the J -dependent RRKM branching ratios and the J -dependent complex formation probabilities. Such a comparison has been performed in this laboratory by Berblinger for HD_2^+ .¹²

Table 6 shows, finally, how the induction time depends on the masses. These data can qualitatively be understood in terms of the momentum exchanged during the first binary encounter, which influences also the complex formation

cross-section.⁹ Indeed, Fig. 6 shows that the induction time is closely correlated with the complex formation cross-section. Simplifying, one can say that equality of the masses of projectile and target atoms decreases the induction time, and that two masses in the diatom cumulate their influence. The value of τ for masses 2, 1, 2 is the only exception to that rule.

In Fig. 6 we have plotted the data *vs.* Mahan's^{13a} parameter [for amplification of this formula, see, for example ref.

Table 4 Influence of total angular momentum on the induction time^a

J range	N	$(\tau \pm \sigma_\tau)/\text{fs}$
0–10	225	22 ± 15
10–20	426	23 ± 10
20–30	479	43 ± 9
30–40	363	253 ± 29

^a Masses 1, 1, 1. $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV. $C_1 = 1/3$ and $C_2 = 2/3$ in eqn. (5). Only trajectories with ≥ 8 minimum exchanges are included.**Table 5** Mass dependence of the asymptotic branching ratio, C_1 , from trajectories with ≥ 30 minimum exchanges with $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV

masses	m_p/m_T^a	N^b	$C_1 \pm \sigma_1$
1, 2, 2	0.25	168	0.44 ± 0.04
1, 2, 1	0.33	56	0.34 ± 0.06
1, 1, 1	0.50	804	0.365 ± 0.017
2, 1, 2	0.67	53	0.30 ± 0.06
2, 1, 1	1.00	154	0.29 ± 0.04

^a Ratio of projectile mass to total target mass: $m_A/(m_B + m_C)$. ^b N is the number of trajectories in the sample.**Table 6** Dependence of asymptotic branching ratio, C_1 , and induction time, τ , on the masses^a

masses	m_p/m_T^b	f_{Mahan}^c	N	$C_1 \pm \sigma_1$	$(\tau \pm \sigma_\tau)/\text{fs}$
1, 2, 2	0.50	0.56	398	0.38 ± 0.08	199 ± 54
1, 2, 1	0.75	0.64	129	0.30 ± 0.08	110 ± 37
1, 1, 1	1.00	0.75	1521	0.37 ± 0.02	65 ± 6
2, 1, 2	1.50	0.77	134	0.35 ± 0.06	46 ± 29
2, 1, 1	2.00	0.89	303	0.23 ± 0.06	139 ± 33

^a $E_{\text{tot}} = E_{\text{tr}} = 0.5$ eV, $C_2 = 1 - C_1$ in eqn. (5). N is the number of trajectories in the sample. ^b The ratio m_p/m_T denotes here the average of projectile mass/target mass, i.e. $1/2(m_A/m_B + m_A/m_C)$. ^c f is Mahan's¹³ parameter describing the fractional energy transfer for collinear impulsive collisions. For heteronuclear targets we take the average of the two values of f . **Fig. 5** Induction time *vs.* total collision energy (cf. Table 3). The kinds of energy supply are: □, only translational, Δ, mostly vibrational; ○, mostly rotational. Filled symbols correspond to case (a) in Table 3, open ones to case (b). The dashed curve is an exponential fit to all points except the two highest marked □.

Fig. 6 The reduced induction time (■, left scale) and the complex formation cross-section σ_c (●, right scale, from ref. 9) vs. Mahan's energy transfer parameter f (see text and ref. 13). To show the similarity, the right scale was shifted and inverted.

13(b) and (c)]

$$f = \frac{4m_A m_B m_C (m_A + m_B + m_C)}{(m_A + m_B)^2 (m_B + m_C)^2} = \sin^2(2\beta) \quad (6)$$

(β being the usual skewing angle), which describes the fraction of energy transferred in a collinear encounter in the impulsive limit. From this point of view, the exception of the rule is mass distribution 2, 1, 1. We suppose, that the impulsive collinear model fails here, because energy transfer to diatomic rotation helps to form the complex fast and efficiently.

Discussion

The detailed investigation of complex collisions in the $H^+ + H_2$ system and its isotopomers has shown that it is possible to define an induction time, which determines the delay that is needed after the first bimolecular encounter to destroy the correlation between the non-statistical motion of the approaching collision partners, and to establish the statistical behaviour of the long-lived complex. We have determined this time from several parameters monitored: relative interatomic distances of the living complexes, and the branching ratios into different channels in complex decay. We have also tried, but mostly in vain, to detect an induction time by looking into the angular distributions of the decaying complexes.

Monitoring the internuclear distances gives the best statistics, since all systems, not only decaying ones, contribute. A gross value for the induction time in $H^+ + H_2$ for collision energies of 0.25–1.5 eV with all energy supplied as translation is 35 fs. Large total angular momenta increase this value, the probability of producing such complexes is, however, small. Unfortunately, an experimental determination of this type of induction time seems unfeasible.

This is not so for the induction time determined from branching ratios of complexes decaying after a given time, which should be measurable with femtosecond techniques (cf. e.g. ref. 14). (One has to find a reaction, which forms complexes only from an excited projectile or target, and monitor the products with the second laser pulse.) Though the error bounds on these data are larger than in the former case, some general trends can be established. The following factors increase the induction time: small collision energy, large total angular momentum, and a large difference in the atomic masses in the first binary encounter. In all these cases, the complex formation cross-section decreases in parallel with

the increasing induction time. The common reason is that the initial energy transfer from the projectile determines both the trapping probability into and the speed of energy equilibration within the complex.

The traditional experimental criterion for complex formation, forward-backward symmetry of the differential cross-section, should be applied with caution. First, it measures at best the lifetime of the complex, not the formation of its energetic equilibrium. Secondly, the timescale applied, i.e. the rotation period of the complex, is an average over a very wide distribution, which is determined by the contributions of different J in the formation of the complexes.

As an aside, we should mention that also the translational energy of the decaying complexes depends on the distribution of J -values in their formation: we have shown (e.g. in ref. 11) that in the limit of large J , the energy stored in the complex is completely needed to overcome the centrifugal barrier, after which it is completely dumped into translation. Therefore, the average outgoing translational energy will depend very much on the probability distribution $P_c(J)$ of forming the complexes, which, in turn varies with E .

With respect to the generality of our results, dimensional analysis shows that all of them should be valid for any triatom of symmetry D_{3h} whose well shape is not too different from that of H_3^+ , if one applies proper scaling. Additional experience with trajectory calculations on collinear H_3^+ (in different isotopic variants) shows that the situation for linear triatomic molecules with 'chemical' internuclear potentials (modelled, e.g., by pairs of Morse potentials between neighbours) is not much different, at least for ABA molecules. So we feel that for triatomic systems with a chemical well and not too different masses our results should be typical: one expects quite generally a timescale of the order of $30\text{--}50(M/3)^{1/2}$ fs for the establishment of the equilibrium in the complexes.

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References

- 1 R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987.
- 2 W. B. Miller, S. A. Safron and D. R. Herschbach, *Discuss. Faraday Soc.*, 1967, **44**, 108; G. A. Fisk, J. D. McDonald and D. R. Herschbach, *Discuss. Faraday Soc.*, 1967, **44**, 228.
- 3 D. Gerlich, U. Nowotny, Ch. Schlier and E. Teloy, *Chem. Phys.*, 1980, **47**, 245.
- 4 C. W. Gear, *SIAM J. Numer. Anal.*, 1964, **2**, 69.
- 5 W. Meyer, P. Botschwina and P. Burton, *J. Chem. Phys.*, 1986, **84**, 891.
- 6 R. K. Preston and J. C. Tully, *J. Chem. Phys.*, 1971, **64**, 4297.
- 7 S. Brandt, *Datenanalyse*, B. I. Wissenschafts-Verlag, Mannheim, 1981.
- 8 M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics*, Griffin, London, 1961.
- 9 Ch. Schlier and U. Vix, *Chem. Phys.*, 1987, **113**, 211.
- 10 Ch. Schlier and U. Vix, *Chem. Phys.*, 1985, **95**, 401.
- 11 Ch. Schlier, *Mol. Phys.*, 1987, **62**, 1009.
- 12 M. Berblinger, Ph.D. Thesis, Freiburg, 1992; M. Berblinger and Ch. Schlier, to be published.
- 13 (a) B. H. Mahan, *J. Chem. Phys.*, 1970, **52**, 5221; (b) M. H. Cheng, M. H. Chiang, E. A. Gislason, B. H. Mahan, C. W. Tsao and A. S. Werner, *J. Chem. Phys.*, 1970, **52**, 6150; (c) V. M. Azriel, L. Y. Rusin and M. B. Sevryuk, *Theor. Chim. Acta*, to be published.
- 14 I. R. Sims, M. Gruebele, E. D. Potter and A. H. Zewail, *J. Chem. Phys.*, 1992, **97**, 4127.