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Lifetimes of triatomic collision complexes

LIFETIMES OF TRIATOMIC COLLISION COMPLEXES

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Received 22 October 1984

Lifetimes of long-lived collision complexes of $\text{H}^+ + \text{H}_2$ and some isotopic variants have been determined from classical trajectory calculations. A lifetime range of 0.1–50 ps could be covered, while a typical vibrational period of the complex is 10 fs. The results agree in general with the expectation from RRKM theory: independence of τ of the origin of the energy of the complex (translation, vibration, or rotation), and a power law dependence of τ on $E/(E + D)$ with exponent 2. A closer look shows a dependence of τ on total angular momentum J , which is also the main reason for non-exponential decay curves of samples for which J is not specified, and for much of the apparent dependence of τ on mass distributions. Our data show that an induction time is needed before the complex obtains its (statistical) properties.

1. Introduction

It is well known that atom–diatom collisions under the influence of a deep potential well will lead to collision complexes, which are long-lived compared to the vibrational period of the quasi-molecule, *if* the total energy of the complex is not too high. In the early days of trajectory calculations, already, there were studies of the lifetimes of these complexes [1,2], and several papers have since appeared, which are relevant to the topic [3–6]. The difficulty is, of course, that we expect the long-lived complex to be “statistical” in its decay, i.e. its decay properties should be independent of the history of its formation (except for conserved quantities like total energy and angular momentum). For the numerical computation this “loss of memory” means an intrinsic loss of accuracy, which can only for some time be counteracted by a small step size in the integrating routine, double-precision variables and the like. It is this effect which practically limits the longest lifetimes, that can be computed by this method, while the shortest ones are determined by the finite time needed to form a complex, i.e. to distinguish it from a direct collision.

In this paper we have used the DIM potential for H_3^+ [7], and different mass combinations of H

and D to compute the lifetimes of $(\text{H}(\text{D}))_3^+$ complexes formed in proton–hydrogen collision (or isotopic variants thereof) at different total energies. The origin of E , i.e. whether it came from translation, vibration, or rotation was also varied. From dimensional analysis it follows that the classical lifetime must have the following functional form

$$\tau = \left(\frac{mr_0}{V_0} \right)^{1/2} \text{fct} \left(\frac{m_k}{m}, \frac{E_k}{E}, \frac{E}{V_0} \right). \quad (1)$$

Here r_0 and V_0 are a typical size and depth of the potential, $E = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}}$ is the total energy, and $m = m_1 + m_2 + m_3$, is the total mass. The dependence of τ on the potential shape has to be understood. If our expectation concerning the statistical nature of the decaying complex is honoured by nature, the dependence of τ on the origin of the energy, i.e. on E_k/E , can be dropped, and τ must be invariant against permutations of the m_k .

Actually we find an additional dependence of τ on total angular momentum J , which is the other quantity conserved through the complex. This dependence has been emphasized [8] and seen in other trajectory calculations [5,6]. It means that we have to replace eq. (1) by

$$\tau = \left(\frac{mr_0^2}{V_0} \right)^{1/2} \text{fct} \left(\frac{m_k}{m}, \frac{E_k}{E}, \frac{E}{V_0}, \frac{J^2}{mr_0^2 V_0} \right), \quad (1a)$$

with the same comments as above. Since different reactant channels (e.g. $\text{H}^+ + \text{D}_2$ versus $\text{D}^+ + \text{HD}$) produce ensembles with different J -distributions, different lifetimes for complexes formed from different channels are possible.

We consider this work as a model study on what happens in a certain type of potential well (characterized by a D_{3h} equilibrium configuration and large anharmonicities) rather than a special study on H_3^+ . For similar potentials, e.g. the usual model potential for Ar_3 (a sum of three Morse functions) very similar results are expected after proper scaling! Since Ar_3 has a well depth of only $\approx 1/250$ of that of H_3^+ this means physically quite a change: complex formation in $\text{Ar} + \text{Ar}_2$ collisions will only happen at sub-thermal energies. Of course, potentials with entirely different shape (e.g. CO_2) must be investigated separately.

The plan of the paper is as follows: section 2 describes our method of calculation and handling of trajectory data. General results will be discussed in section 3.1 followed by chapters on the influence of angular momentum on lifetimes (section 3.2) and on isotope effects (section 3.3). The paper is closed in section 4 with some general comments and conclusions.

2. Method

The computations were performed with our standard trajectory program [9,10]. Batches of 1000 trajectories were started for each set of initial conditions (masses, energies). Irrelevant initial conditions were Monte Carlo selected, including the impact parameter weighted $\propto b db$ to allow the extraction of complex-formation cross sections σ_c . b_{max} was always taken large enough so that no complex collisions were missed. In some cases b was fixed in order to define the total angular momentum. In these cases only the complex formation probability $P_c(b)$ can be extracted, not a cross section.

We defined a long-lived complex as in our earlier papers [9,10] by counting the number of

minimum exchanges, i.e. the number of times, where $\min(R_{AB}, R_{BC}, R_{CA})$ changes its identity. We have shown in a former paper [11] that requiring at least 8 minimum exchanges is practically equivalent to other definitions in the literature. Applied to lifetimes we may state that for sufficiently long-lived trajectories the extracted lifetime is strictly independent of the exact number of minimum exchanges used in its definition. Our definition implies that it needs some time until all long-lived complexes have been formed, i.e. until we can decide whether a trajectory is complex or rather “direct” or “peripheral” [9]. On the other hand a trajectory need not be finished in order to use it in the determination of the lifetime, and we stop computation generally after 800 fs.

In practice we plot the number of living complexes, i.e. the number of all complexes (which is known after waiting long enough) minus the number of decayed complexes, versus time in a log-log plot. Two examples are shown in fig. 1. We have to exclude an induction period, in which trajectories exist of which it is undecided whether they will be complex or not. This behaviour can be seen from the curves plotted with plus signs (+) in fig. 1a. The rest of the points is linearly fitted to extract τ . Inspection shows that for most cases an exponential decay law is well complied with. A counterexample is shown in fig. 1b, and discussed below.

Alternatively the lifetime of a trajectory can be defined as the time interval between the first and last minimum exchange. A similar definition has been used in refs. [4,5]. If the random-lifetime assumption holds the differential as well as the integral probability distributions should follow an exponential law. The latter is shown additionally in fig. 1a, it is much less prone to scatter than the differential curve, and can be directly compared with our usual method of evaluation. This figure and other examples show that the two methods give equivalent results if the induction period, which contains undecided complexes in the first case and direct collisions in the second, is treated properly.

Before we close this section we must discuss the accuracy of the calculations. We have noted above the general problem of numerically following

Fig. 1. (a) Formation and decay of complexes for masses 2, 1, 2; $E = E_{tr} = 1.0$ eV. Points (●) show the number of complexes evaluated as described in the text. Plus signs (+) show the genesis of the complexes: the upper curve includes all complexes (including decayed ones), the lower only those not yet decayed. Crosses (×) show the integral distribution of lifetimes measured between the first and the last minimum exchange (see text). The initial part is influenced by direct collisions. Straight lines are exponential fits to the points $300 \leq t \leq 800$ fs and $200 \leq t \leq 700$ fs for the first (●) and second (×) method, respectively. The lifetime constants given by these fits are 610 and 640 fs, respectively. (b) Decay of complex of masses 2, 1, 2; $E = E_{tr} = 0.5$ eV. Points (●) show all complexes formed. The decay is non-exponential because the sample is a mixture of different J (see text). Taking that half of the complexes with J smaller than the median value (lower points marked ×) we get a decay which is exponential within errors, whereas the upper half (×) is still non-exponential, i.e. consists of a sufficiently non-uniform sample with respect to τ . Straight lines are drawn to guide the eye. The logarithmic scale is exaggerated three times with respect to the left-hand panel and the partial decay curves are shifted by a factor $10^{1/3}$ to avoid congestion of points.

chaotic trajectories for long times. One has to be careful that τ measures a mechanical property of the system, and not a numerical property of the integrating routine. The often heard argument that it does not matter whether one has long term

numerical accuracy if the system is “statistical” sounds intriguing but does not prove anything. Mathematically it can be shown to hold under certain assumptions [12], which, however, are difficult to apply to realistic systems and do not strictly apply here. As is well known, energy conservation does not prove the accuracy of numerical integration. (We have observed that E oscillates about the exact value during integration, indicating a certain stability of the integrating routine with respect to energy conservation, even if the trajectory went grossly astray from the true one.)

The accuracy parameters of our integration routine was therefore fixed by demanding that the complex decay curves $N_c(t)$ be reproducible. This accuracy ensures back integrability to ≈ 500 fs but in some cases not to the end of our trajectories. It meant a parameter 10^{-4} times that used in our former calculations, where only a complex-formation cross section had to be extracted. Computation times were ≈ 15 times longer than before, i.e. ≈ 100 h on a PE 3220 for a batch of 1000. The lifetimes reported in our earlier paper [9] are incorrect because the trajectories were cut off too early, not because the accuracy of integration failed.

3. Results and discussion

3.1. General results

Our first two sets of calculations consisted of 10 calculations for masses 1, 1, 1 (i.e. $H^+ + H_2$), and 14 for masses 1, 2, 2. The results are plotted on log-log scales in figs. 2 and 3 versus the parameter $z = E/(E + D)$, where E is the total energy, and D is the depth of the triatomic well. The zero of energy is at the equilibrium of the diatom with the ion at infinity. Since we are using classical dynamics we consider zero-point energies as normal vibrational excitation. The statistical (fitting) errors of the single lifetimes are a few percent except for the lowest energies, where some error bars are shown in the figures. We have fitted the points of figs. 2 and 3 to the power law

$$\tau = \tau_0 z^{-s} \quad (2)$$

with $z = E/(E + D)$, which is what RRKM theory

Fig. 2. Lifetime of H_3^+ complexes versus the RRKM-parameter $z = E/(E + D)$. The marks indicate the origin of E : $\square$ only translational, ∇ mostly vibrational, $\circ$ mostly rotational. The straight line is a fit to eq. (2) with $\tau_0 = 14.7$ fs, $s = 1.90$.

predicts [13–15]. Here s is the (effective) number of vibrations minus one, which we can expect to be 2 or 2.5 depending on the activity of one of the rotational degrees of freedom of the complex, and τ_0 is the usual ratio of vibrational frequencies, which should be of the order of a typical vibrational period of the complex (10–20 fs). Results for s and τ_0 are presented in table 1.

Calculations for other mass combinations were only made at energies $E = E_{\text{tr}} = 0.25, 0.5$, and 1.0 eV, and evaluated in a similar way.

The following observations can be made from the data in figs. 2 and 3, and from table 1:

(1) Lifetimes are almost independent of the way the energy is supplied to the complex, i.e. of whether the energy comes from translation, vibration, or rotation. A small effect in the sense that

Fig. 3. Same as fig. 2 for HD_2^+ complexes. Fit to eq. (2) with $\tau_0 = 13.5$ fs, $s = 1.97$.

complexes produced from internally excited targets have shorter lifetimes is statistically significant. For an explanation see below.

(2) The exponent s from the fit to the RRKM

Table 1

Parameters in the lifetime formula, eq. (2), for different mass combinations and initial conditions (trans: E is translational only, int: $E_{\text{int}} = E - 0.1$ eV). The number of fitted points is N . Statistical errors are typically 6% for s and 30% for τ_0

m_k	E	N	s	τ_0 (fs)
1, 1, 1	all	10	1.90	14.7
	trans	6	1.86	17.9
	int	4	1.85	13.9
2, 1, 1	trans	3	2.14	12.0
1, 1, 2	trans	3	1.84	24.8
1, 2, 2	all	14	1.97	13.5
	trans	6	2.02	12.7
	int	8	1.77	19.7
2, 1, 2	trans	3	2.05	17.9

form has very nearly the expected value 2. This is in accord with the intuitive understanding that in a system like H_3^+ no “inactive” vibrations exist, and shows that both rotations of the complex are inactive.

(3) A dependence of lifetimes on the atomic masses involved can be seen. This is discussed in section 3.3.

3.2. The role of angular momentum

Even if a sufficiently long-lived complex loses all of its “memory” due to strong interaction it cannot “forget” total angular momentum, since this is conserved. Our batches of trajectories are, therefore, not homogeneous, and even if the random lifetime hypothesis holds for complexes characterized by E and J , it must not hold for mixtures, if only τ is a function of J . This possibility has been discussed in the literature on unimolecular decay [13,14], and was recently stressed by Quack and Troe [8]. A dependence of τ on J (or rather b , which is generally equivalent) has been reported in refs. [5,6]. (These calculations are, however, not easily compared with ours.)

The numbers discussed so far in table 1 are, therefore, averages

$$\bar{\tau} = \int \tau(J) P_c(J) dJ, \quad (3)$$

where $P_c(J)$ is the probability that a complex is formed with angular momentum J . It is easy to

see that this distribution must depend on the initial state, even if the total energy E is kept fixed: for a well potential the largest J leading to complex formation is limited by the Langevin condition that the system overcome the centrifugal wall, which in practice is a function of E_{tr} only. Let, e.g., a greater part of E be supplied via target vibration. This means E_{tr} , and with it J_{max} , must decrease, so $P_c(J)$ will be limited to a smaller range of angular momenta than before. Since, as we will see, τ is an increasing function of J , this explains the observation made above that $\bar{\tau}$ is somewhat smaller if the energy is supplied with a larger share of target excitation.

Still, most of our decay curves $N_c(t)$ versus t do not visibly deviate from an exponential, i.e. from a straight line in a log-log plot. (For an exception see fig. 1b.) But if we divide our trajectories into subgroups arising from different ranges of impact parameter b , equivalent to different total angular momenta, we find that *all* batches show a dependence of τ on J . Taking b -intervals which are quarters of $0-b_{\text{max}}$ the spread of τ is between 1:1.5 and 1:5 depending on masses and other initial conditions (e.g. larger spread for smaller total energy).

To discuss this dependence with more precision it is advisable to compute lifetimes of ensembles in which E and J have been fixed. A first example is shown in table 2. We compare properties of complexes formed of masses 1, 1, 2, energies $E_{\text{tr}} = 0.1$ eV, $E_{\text{vib}} = 0.4$ eV, $E_{\text{rot}} = 0$ at fixed values of J .

Table 2

Dependence of some properties on total angular momentum for a typical complex. Initial conditions: $m = 1,1,1$; $E = 0.5$ eV, $E_{\text{tr}} = 0.1$ eV, $E_{\text{vib}} = 0.4$ eV; $j = 0$. Initial values of b and J are indicated in columns 1 and 2 respectively. P_c is the complex formation probability, τ the lifetime. Other properties are known only for completed trajectories (whose fraction at 800 fs has been indicated in column 5): $\langle \Delta t \rangle$ is the average time between two minimum exchanges, which can be thought of as a measure for the vibrational period, $\langle \Delta j \rangle$ the average rotational excitation, $\langle E'_{\text{rot}} \rangle$ the average final rotational energy. The last line contains typical standard deviations

b (Å)	J ($\hbar$)	P_c (%)	τ (fs)	Completed (%)	$\langle \Delta t \rangle$ (fs)	$\langle \Delta j \rangle$ ($\hbar$)	$\langle E'_{\text{rot}} \rangle / E$ (%)
0–4.67	av 19.3	av 90	111	38	8.3	5.0	31
0.4	2.5	89	61	62	8.5	4.1	23
2.3	14.2	91	106	38	8.1	5.2	33
4.2	26.0	85	143	30	8.2	4.5	26
std. dev.	–	1	4	–	0.1	0.1	2

These are ≈ 0.1 , 0.5 , and 0.9 times the maximum J occurring in the mixed sample, whose properties are also given. One sees that most of the properties do not depend very much on J . The most obvious difference in behaviour is that between P_c and τ . While the probability of complex formation is approximately constant for low and medium values of J , and begins to drop at $J = 26$ (it will be zero at $J = 29$), the lifetime is an almost linear function of J . (It may turn out to be non-linear like that of ref. [5], when more points will be computed.) As a consequence of the fixed time of 800 fs at which all trajectories are stopped, the number of completed trajectories depends heavily on J . But it is remarkable how similar other properties are. Take rotational excitation as an example: it is true that $\langle \Delta j \rangle$ is significantly different for the three initial conditions. It drops somewhat when $J \rightarrow 0$, probably because the average torque decreases. It drops also when $J \rightarrow J_{\max}$ and will be zero for $J \gg J_{\max}$. But the spread is only 25% compared to 230% for τ . Apparently the lifetime is quite singular in its dependence on the angular momentum.

The data on $\tau(J)$ obtained here are not sufficient for a general comparison with theories incorporating J into the general RRKM scheme. An additional handicap comes from the fact that many parameters needed in these theories are difficult to obtain with sufficient precision without extensive numerical computation. So we have only explored whether it might be sufficient to correct the available energy E in eq. (2) for the J -dependent height of the outbound centrifugal wall, $E_{\max}(J)$. This can be done by replacing E in formula (2) by $E - E_{\max}$, which leads to

$$\tau(J)/\tau(0) = (1 - E_{\max}(J)/E)^{-2}. \quad (4)$$

$E_{\max}$ can be computed with sufficient accuracy as the maximum of the average effective potential for outbound motion, which may be written

$$\begin{aligned} V_{\text{eff out}} &= V(r) + J^2/2\mu r^2 \\ &= V(r) + E_{\text{tr in}} b_{\text{in}}^2/r^2. \end{aligned} \quad (5)$$

Here, $V(r, \vartheta)$ has been averaged to $V(r)$, L_{out}^2 has been approximated by J^2 , and for the second equality we have used that $J_{\text{in}} = L_{\text{in}}$ since $j = 0$. In

practice $E_{\max}$ can be found from the knowledge of the “capture” impact parameter b_c as function of E_{tr} : $E_{\max}$ is the solution of

$$Eb_c^2(E) = E_{\text{tr in}} b_{\text{in}}^2. \quad (6)$$

It goes without saying that $b_c(E)$ has to be taken for the potential used in the trajectory calculations, and this cannot be substituted by the polarization potential of the system.

The result of our investigation was negative: reducing the available energy in the RRKM formula by the height of the centrifugal wall is insufficient to explain the strong dependence of τ on J . So we have to expect further computations of $\tau(J)$ to find out what the main reason for this dependence might be.

3.3. Isotope effects

There are three ways in which the lifetime may depend on the masses involved, given the potential and the energies:

(a) The whole time scale is proportional to $m^{1/2}$ where m may be taken as total mass or another typical mass.

(b) Lifetime may depend on mass distribution. Our expectation that the complex “forgets” its origin means, however, that τ should be invariant against permutations of the three masses.

(c) The average lifetime, eq. (3), depends on $P_c(J)$, which will in general depend on the mass distribution involved. Here, even the invariance mentioned under (b) cannot be expected.

Table 3

Lifetimes of complexes of different masses at $E = E_{\text{tr}} = 0.5$ eV. We show the values fitted to the data at $E = 0.25, 0.5$, and 1.0 eV only. The value for masses 2, 2, 2 has been computed from 1, 1, 1

m	m_k	$\tau(\text{fs})$	$\tau/m^{1/2} (\text{fs})$
3	1,1,1	170	98
4	2,1,1	196	98
4	1,2,1	196	98
5	1,2,2	149	67
5	2,2,1	236	106
6	2,2,2	240	98

Table 4

Cross sections and lifetimes for complexes of pairwise equal masses but originating from different channels. $E = E_{tr} = 0.5$ eV. m is total mass, μ the reduced mass of the projectile-target system. Mixed J ensembles contain all impact parameters leading to complex formation in the channel involved, weighted $\propto b db$, whereas in the ensembles with $J = 40 \hbar$, the value of b has been taken $\propto \mu^{-1/2}$

m	m_k	μ	Mixed J		$J = 40 \hbar$		
			$\sigma_c (\text{\AA}^2)$	τ (fs)	$b(\text{\AA})$	P_c (%)	τ (fs)
4	2,1,1	1	21.9	195 ± 10	2.586	50.4	337 ± 5
4	1,1,2	0.75	28.8	235 ± 14	2.986	86.6	390 ± 25
5	1,2,2	0.8	22.7	163 ± 30	2.891	49.3	196 ± 5
5	2,1,2	1.2	30.9	270 ± 30	2.361	75.3	244 ± 5

In the RRKM formulation, eq. (2), effects (a) and (b) are contained in τ_0 , whereas (c) is neglected.

Isotope effects have great influence on the cross sections for complex formation as we have discussed in another paper [16]. Table 1 shows that there is also a small effect on lifetimes. Table 3 shows a set of lifetimes at $E = 0.5$ eV, which allows better comparison because the values have been fitted to the results obtained at three energies. These data show that the mass dependence is not merely given by effect (a) above, and that the lifetimes of the “same” complexes, e.g. with masses 2, 2, 1 and 1, 2, 2 are not equal.

To find out how much of this difference can be explained by the different J -distributions in different initial channels, we have performed one further calculation at fixed J , which is displayed in table 4. It can be seen that there is still no complete independence of τ from the masses of initial channel though the differences are less than 20% now. At the moment we cannot but call this an example of non-RRKM behaviour. It fits to other observations showing that complex “forgets” very slowly which of the three atoms was the projectile. This is commented further below.

4. Concluding remarks

In this paper we have calculated lifetimes of long-lived complexes of H(D)_3^+ from trajectories run on a model potential (DIM) for that molecule. The complexes were formed by collisions, i.e. by “chemical activation”. A collision energy range of 2–20% of the well depth has been covered leading to average lifetimes of typically 2000–20 vibra-

tional periods of the complex. Trajectories were integrated up to ≈ 100 such periods, beyond which it was not possible to ascertain that the properties computed are those of the complex rather than those of the integrating routine.

Most of our lifetime distributions are exponential within the time limit just mentioned. All deviations from the exponential decay law could be attributed to (a) a strong dependence of lifetime on angular momentum, which makes the chemically activated complex an inhomogeneous sample, and/or (b) induction effects.

It is important to recognize that there must be an induction period between the time of the first near encounter of A with BC (the time at which A “reacts” with BC), and the time at which we can speak of a long-lived complex, which has statistical properties and decays exponentially. This is not a formal argument suggesting that the observer can decide about direct or complex collisions only after the fact. (Note that “direct” in our language includes an appreciable amount of migration.) It rather means that the strong interaction leading to the mixing of modes in the activated molecule needs time for this coupling to happen. A similar situation exists for overtone excitation, while the situation is, of course, different for direct microcanonical excitation of the complex.

Repeating the argument in the language of trajectories, the exponential divergence discriminating a “regular” from an “irregular” trajectory is different from a linear divergence only after some finite time, taking into account that the divergence itself is a random variable. The stochastic impulse in the sense of ref. [17] must be collected before it implies that neighbouring trajec-

ries have been widely separated. Or, stated in anthropomorphic terms, the complex needs time to forget its origin.

Some of these concepts have been put between quotation marks because it should be clear that concepts of ergodic theory are, strictly speaking, not applicable to collisional systems because their phase space is not compact [11]. They may, nevertheless, be a good, even the best way to speak about long-lived complexes, but they are certainly already approximate concepts. Strictly speaking, all our trajectories are regular, and it is only by applying some coarse graining that they resemble irregular ones.

The time after which in practice statistical behaviour is achieved, is not only finite but also dependent on the property for which one asks. So one knows that vibrational equilibration can be very fast (see ref. [18] for an example where a "complex" is barely formed). It can be much faster than the equilibration of rotational angle (mod 2π), which experimentalists take so often as the only indication for complex behaviour. We have noted on the other hand that it needs quite a long time (typically 20 rather than 8 minimum exchanges) before the trajectories forget which atom was the projectile, i.e. before the decay into channels AB, BC, and CA proceeds with the same rate. Still more extreme would be the time scale on which nuclear spin takes part in equilibration, i.e. on which a complex "forgets" whether it came from $H^+ + o\text{-}H_2$ or $H^+ + p\text{-}H_2$ [19].

With regard to non-RRKM behaviour the abovementioned situations means that we must either call all chemically activated complexes non-RRKM ones, or (which we prefer) exclude the induction period from the tests for such behaviour. The length of this period will certainly depend on the strength of the coupling, i.e. on potential shape, energies and the like. We may also expect a hierarchy of different time scales for the induction times with respect to different properties of the complex.

Another question which we want to address here is the relation between complex-formation probability (or cross section if the J -average is taken), and complex lifetime. It has been argued that both properties contain "fundamentally the

same" information [5]. But this is not so in practice. Complex-formation cross sections refer generally to a *certain* initial state, or a predetermined group of each states, while the decay goes into *all* accessible states. Microscopic reversibility, however, connects only the probability of complex formation from a certain region of phase space with the decay probability into the *same* region of phase space. But the latter is different from the average decay probability implicit in the lifetime. Empirically we find, nevertheless, a good correlation between large complex-formation cross sections and short lifetimes. It is, however, neither quantitative nor without counter-examples as can be seen from tables 2 and 4.

Acknowledgement

We thank J. Troe and D. Gerlich for clarifying discussions. The support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- [1] D.L. Bunker, J. Chem. Phys. 37 (1962) 393; 40 (1964) 1946.
- [2] W.L. Hase, in: Modern theoretical chemistry, Vol. 2B, ed. W.H. Miller (Plenum Press, New York, 1976).
- [3] R.J. Wolf and W.L. Hase, J. Chem. Phys. 72 (1980) 316; W.L. Hase and R.J. Wolf, J. Chem. Phys. 75 (1981) 3809; W.L. Hase, R.J. Důchovic, K.N. Swamy and R.J. Wolf, J. Chem. Phys. 80 (1984) 714.
- [4] K.N. Swamy and W.L. Hase, J. Chem. Phys. 77 (1982) 3011.
- [5] L.M. Babcock and D.L. Thompson, J. Chem. Phys. 78 (1983) 2394.
- [6] J.A. Miller and N.J. Brown, J. Phys. Chem. 86 (1982) 772.
- [7] R.K. Preston and J.C. Tully, J. Chem. Phys. 64 (1971) 4297.
- [8] M. Quack and J. Troe, Ber. Bunsenges. Physik. Chem. 78 (1974) 240; M. Quack and J. Troe, in: Gas kinetics and energy transfer, Vol. 2, eds. P.G. Ashmore and R.J. Donovan (Chem. Soc., London, 1977); J. Troe, J. Chem. Phys. 79 (1983) 6017.
- [9] D. Gerlich, U. Nowotny, Ch. Schlier and E. Teloy, Chem. Phys. 47 (1980) 245.
- [10] Ch. Schlier, Chem. Phys. 77 (1983) 267.
- [11] Ch. Schlier, in: Energy storage and distribution in molecules, ed. J. Hinze (Plenum Press, New York, 1983).

- [12] G. Benettin, M. Casartelli, L. Galgani, A. Giorgilli and J.-M. Strelcyn, *Nuovo Cimento* **44B** (1978) 183.
- [13] D.L. Bunker, *Theory of elementary gas reaction rates* (Pergamon Press, Oxford, 1966).
- [14] W. Forst, *Theory of unimolecular reactions* (Academic Press, New York, 1973) ch. 7.
- [15] J. Troe, in: *Physical chemistry, an advanced treatise*, Vol. 6B, ed. W. Jost (Academic Press, New York, 1975).
- [16] Ch. Schlier and U. Vix, to be published; U. Vix, *Zulassungsarbeit*, Freiburg (1981).
- [17] J.S. Hutchinson and R.E. Wyatt, *J. Chem. Phys.* **70** (1979) 3509.
- [18] M.K. Osborn and I.W.M. Smith, to be published.
- [19] D. Gerlich and H.J. Bohli, in: *Book of abstracts, European conference on atomic physics*, eds. J. Kowalski, G. zu Putlitz and H.G. Weber (European Physical Society, Heidelberg, 1981).