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Complex formation in proton-hydrogen collisions
II. Isotope effects

COMPLEX FORMATION IN PROTON–HYDROGEN COLLISIONS. II. ISOTOPE EFFECTS

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Classical trajectory calculations have been performed on the DIM potential energy surface of $H^+ - H_2$ for collision energies between 20 meV and 2 eV. Complex formation cross sections have been determined for many combinations of projectile and target masses, showing that capture behind the centrifugal barrier is a necessary but by no means sufficient condition for the formation of a long-lived complex. Its probability depends on energy and masses in a way which suggests that the initial energy loss of the projectile on its approach to, and first encounter with the target plays a crucial role in the “trapping” process. H/D isotope effects exceed 20% at energies above 1/20 of the potential well depth, and reach more than 200% at higher energies. At collision energies below 1/100 of the well depth the isotope effect disappears, and the complex formation cross section becomes equal to the capture cross section *if* the target has no (classical) internal excitation. If, on the contrary, the target is internally excited this equality is invalidated, and an isotope effect of a few percent due to different zero point energies remains. Microreversibility arguments show that these effects should have a perceptible influence on the results of a “dynamically biased” phase space theory.

1. Introduction

A general theory of isotope, or, more generally, mass effects in reactive collisions has not been given so far, and probably never will. Too different are the mechanisms ruling the reactive process, and each will have its specific way, by which it responds to changes of the reactant masses. The only exception is the general statement from dimensional theory that reaction cross sections in a classical theory will not depend on the mass *scale* (i.e. on a common mass factor), other things being equal. This restriction does not only mean that one uses the same potential surface, but also that one employs a reduced energy scale, e.g., that one measures all energies in units of the potential well depth. For a specific reaction mechanism, on the other hand, things look more hopeful: a theory, or at least a general set of rules describing the mass effects should be possible.

In this paper we discuss the mass effects for those $A + BC$ reactions that proceed via a long-lived collision complex. With this we mean a reaction which can be decomposed into two inde-

pendent steps: a step of complex formation, and a step of (unimolecular) complex decay, which are separated by a time interval large compared with the duration of a direct reaction. Both steps are related by microreversibility, thus the mass effects of the latter can be calculated from those of the former, *if* these are known for *all* channels at a given total energy. In general, however, even large mass effects in complex formation can be washed out in complex decay by the contributions of a great number of other channels. In this case the total reaction cross section of a complex reaction will show mainly the mass effects of complex formation, not those of complex decay.

Specifically, this paper gives results obtained from classical trajectory calculations on mass effects of complex formation in the $H^+ + H_2$ system. Since not only the masses but also the energies of the collision may be scaled without influencing the (classical) cross sections, and scaling of the length unit will give a trivial factor, this system may be seen as a model system for many more reactions including neutral ones like, e.g., $Ar + Ar_2$. We have, therefore, also taken the liberty

to use mass values for hydrogen nuclei, which do not exist in nature, including fractional ones. It should be understood from the foregoing, that our model requires that the contribution to the reactive cross section from direct collisions must be small, if one wants to compare the results with experiments. In our system, this requires that the collision energy E (not the total energy!) does not exceed about one third of the well depth.

Isotope effects of ion-molecule reactions proceeding via a long-lived collision complex have not too often been discussed. In 1964 a pioneering paper of Klein and Friedman [1] treated the isotope effect of rare-gas ion reactions with HD, and identified a "displacement isotope effect" of complex formation, and "decomposition isotope effect" of complex decay. The latter seems quite natural nowadays, and can be handled by any of the statistical methods used to model unimolecular decay (RRKM, adiabatic channel, or phase space theory, which is the usual choice for ion-molecule reactions.) In contrast, an isotope effect of complex formation is seldom assumed, because this is commonly regarded as being controlled by "capture" behind the centrifugal wall, and the capture cross section is, in turn, computed with a spherically averaged intermolecular potential, which does not produce any isotope effect. We will discuss these assumptions in detail in the next section.

A review of isotope effects in ion-molecule reactions is contained in a paper by Klein [2]. The intramolecular isotope effect of the $Kr^+ + HD$ reaction was discussed by Hierl [3], but his treatment presupposes that the reaction is direct. More recently, inter- and intra-molecular isotope effects of the $C^+ + H_2$ (D_2 , HD) reaction have been discussed by Armentrout [4]. Using conventional phase space theory to compute the cross sections, he finds a negligible effect in contradiction to experiments [5].

The plan of the paper is as follows: After some general remarks on capture and complex formation we will report on our method of computation (section 3), and our results (section 4). These results can be rationalized by saying that – notwithstanding the necessity that the centrifugal barrier must be surmounted – the probability of

complex formation is essentially a function of the energy deposited in the first encounter of the projectile with the target, which, in turn, is largely influenced by the mass ratios of the reactants. Conclusions and generalizations finish the paper (section 5).

2. Complex formation and capture

State-to-state cross sections of an arbitrary reaction can be parameterized into a direct and a complex contribution [6], viz.

$$\sigma_{i \rightarrow f} = \sigma_{i \rightarrow f}^d + \sigma_{i \rightarrow f}^c, \quad (1a)$$

$$\sigma_{i \rightarrow f}^c = \sigma_{i \rightarrow c} P_{c \rightarrow f}, \quad (1b)$$

where σ^d is the direct cross section, $\sigma_{i \rightarrow c}$ is the complex formation cross section from state i , and $P_{c \rightarrow f}$ is the probability of decay from the complex into state f . In our example i and f stand for channel number α , vibrational quantum number v , and rotational quantum number j of the diatom.

In what follows the direct part of σ will be discarded. It is negligible if two conditions are met: (1) The collision energy must be less than a certain fraction of the well depth of the potential. In our case the well depth D_e is 4.92 eV (measured like all energies from the bottom of the entrance valley, i.e. from the equilibrium energy of $H^+ + H_2$), and the condition for $\sigma_d \ll \sigma_c$ is that approximately $E < 1.5$ eV (cf. fig. 4 of ref. [7] *). (2) Even if internal energy of the target suppresses complex formation much less than collision energy, it must not become comparable to D_e if complex formation is to take place.

The separation of the direct from the complex part of a reaction cross section is, of course, a question of definition. We demand that a "long-lived complex" should have, above all, the property that before it decays it has "forgotten" the initial state from where it comes, except the conserved quantities total energy, E_{tot} , and total angular momentum, J . This is expressed by the

* Ref. [7] is part I of this series.

factorization in eq. (1), which, more precisely, should read

$$\sigma_{i \rightarrow f}^E = \sum_J (2J+1) \sigma_{i \rightarrow f}^{EJ}, \quad (2a)$$

$$\sigma_{i \rightarrow f}^{EJ} = \sigma_{i \rightarrow c}^{EJ} P_{c \rightarrow f}^{EJ}, \quad (2b)$$

where the superscripts indicate conserved quantities.

This definition must be made operational before any calculation can be done, and we have used again [7] the count of “minimum exchanges” during the collision in order to draw the borderline. A minimum exchange is defined as the change of the identity of the smallest of the three internuclear distances, i.e. of $R_{\min} = \min(R_{AB}, R_{BC}, R_{CA})$. It is a convenient measure of what one loosely calls “strong interaction”, and very practical, because the number of minimum exchanges is dimensionless, and therefore invariant against changes of the mass or any other scale. A pair of minimum exchanges is approximately equivalent to one inner turning point of R_{\min} . Our standard borderline, above which we call a collision a complex one, is $N \geq 8$ minimum exchanges, and we have formerly shown [8] that this criterion is equivalent to others based, e.g., on the exponential divergence of neighbouring trajectories. A further discussion of the value of N necessary for the loss of memory can be based on trajectories, which have been computed through the complex until it decays. In this case one can check on all those properties of the products, which should be “statistical” after a complex collision. This leads to the definition of an “induction time” necessary before a decay property is constant, which may even be property dependent. We are preparing a separate paper on this [9]. The results show again, that the number of minimum exchanges needed is between 8 and 25. For the purpose of this paper we fix N to be ≥ 8 , and remark that none of our qualitative results will be different with any other N exceeding 5.

The independence of the decay probabilities $P_{c \rightarrow f}$ from the formation cross sections $\sigma_{i \rightarrow c}$ is further limited by microreversibility. Indeed, if one knows the whole set of $P_{il \rightarrow f}^{EJ}$ for given E and J , and with the label i now *supplemented* by the

orbital angular momentum l , one can write [8]

$$\sigma_{i \rightarrow c}^{EJ} = (\pi/k^2)(2j+1)^{-1} \sum_l P_{il \rightarrow c}^{EJ} \quad (3a)$$

and

$$P_{c \rightarrow f}^{EJ} = \sum_l P_{fl \rightarrow c}^{EJ}, \quad (3b)$$

with the *same* set of P s. It is therefore possible to improve on the phase space theory by using the P s to obtain what we have called [8] the “most dynamically biased” statistical theory. This becomes practical by noting that the P s are smooth functions of their index parameters. In this paper, however, we will not discuss this further, and all cross sections are averages over the possible angular momenta.

In view of some literature discussion we want, however, to stress that the effect of microreversibility is smeared out to a large extent, when only $\sigma_{i \rightarrow c}^E$ and $P_{c \rightarrow f}^E$ are compared, i.e. if one takes averages over J and l . So, if for a given total energy E_{tot} a state v, j has a large cross section to form a complex, there will be some propensity *but not more* that this state is predominantly populated in complex decay. How much this will be the case, depends not only on the complex formation cross section of the state in question, but also on that for any other state competing in the decay.

Let us now discuss another entity, the “capture” cross section σ_L (L for Langevin). For a spherically symmetric potential it is easily defined and computed (in general: numerically) if it exists. For a potential with a repulsive core this is only the case below some limiting collision energy. For a non-spherical potential and non-rigid target things may become much more complicated. We have discussed that in another paper [10], cf. also the work of Chesnavich [11] and Rynefors [12]. In this paper we will use σ_L only as a *reference* cross section, and we *define* it by an approximate formula, which catches the intuitive content of “capture”. It is valid in the adiabatic approximation (fast target rotation) [10], viz.

$$\sigma_L = \frac{1}{3} \sigma_{Lp} + \frac{2}{3} \sigma_{Lo}, \quad (4)$$

where σ_{Lp} is the capture cross section of the planar problem with initial velocity parallel to the

J -vector of the target molecule, and σ_{L0} the same for the orthogonal case. As a further approximation we have taken the potentials with $r = r_e$, and averaged the angular dependence of potential $V_0(R)$, which is not rotationally symmetric, i.e. we take

$$V_p(R) = V(R, r_e, \pi/2), \quad (5a)$$

$$V_0(R) = \frac{1}{2\pi} \oint V(R, r_e, \vartheta) d\vartheta. \quad (5b)$$

This is, again, in the sense of an adiabatic approximation.

The centrifugal barrier for the calculation of both capture cross sections has been taken as the maximum of

$$V_{\text{eff}}(R) = V(R) + L^2 / (2\mu_{A,BC} R^2 + 2\mu_{BC} r^2), \quad (5c)$$

where the additional moment of inertia in the denominator takes care of the fact, that the lowest centrifugal barrier at given energy occurs if the triatomic system rotates rigidly [11–13] *. This choice, like any other choice which takes into account the coupling of orbital and target angular momenta, leads to an isotope effect of the capture cross section. It is, however, small, since typically $r \ll R$. The mass dependence of σ_L can, therefore, be fitted very well (correlation coefficient $r > 0.9997$) by

$$\sigma_L = \sigma_L(0)(1 + \alpha\mu_{BC}/\mu_{A,BC}), \quad (6a)$$

where α is a constant between 0.0093 for $E = 0.02$ eV and 0.051 for $E = 1.0$ eV. The value of $\sigma_L(0)$ for vanishing moment of inertia of the target can further be fitted ($r > 0.9995$) to

$$\sigma_L(0) = 25.40 E^{-0.4258} \text{ \AA}^2, \quad (6b)$$

where E is in eV. The error of these fits is generally below 1%, but we have used the original values when we make reference to capture cross sections.

3. Computations

Trajectories were run in batches of 1000 with the program described earlier [7], which is an offspring of Bunker's "ABC" program. The accuracy parameter of the Gear integrator was adjusted to make trajectories with up to 12 minimum exchanges back-integrable. Initial conditions were Monte Carlo sampled. The maximum impact parameter was set for each energy to be slightly larger than the capture limit. Most calculations were done with no initial internal energy, which we denote by writing $v = -1/2$, $j = 0$. The masses are stated as m_A, m_B, m_C , where m_A is the projectile mass, e.g., 1, 2, 2 means the $H^+ + D_2$ collision. There are two dimensionless mass ratios, which we employ:

$$\delta = \frac{\Delta r}{r_e} = \frac{m_B - m_C}{m_B + m_C}, \quad (7)$$

describing the asymmetry of the target (Δr is the distance from the midpoint of r to the center of mass), and

$$f = \frac{4m_A m_B m_C (m_A + m_B + m_C)}{(m_A + m_B)^2 (m_B + m_C)^2}. \quad (8)$$

f is Mahan's parameter [14] describing the fraction of energy transferred from the projectile to the diatomic target in a *collinear impulsive* collision. It equals $\sin^2 2\beta$, where β is the usual skewing angle. For asymmetric targets, where $f_{ABC} \neq f_{ACB}$, we have taken their average.

Three sets of calculations have been done: The first computes σ_c for 7 mass combinations in the energy range 0.1–2.0 eV. No internal energy is provided. The second set uses all combinations of projectile masses 0.5, 1, 2, 4 with target masses 2–2, 1.8–1.2, 2–1, and 3–1, at collision energies of 0.5 and 1.0 eV. At 0.5 eV a calculation with $v = 2$ is added, also some cases with rotational excitation. The third set contains combinations of projectile masses 1 and 2 with targets 2–2, and 2–1 at collision energies 0.05 and 0.02 eV, where the equality $\sigma_c = \sigma_L$ becomes approximately valid.

* Ref. [13] gives the clearest account of the situation.

4. Results

The outcome of the first set of calculations is displayed in fig. 1. To show the mass effects clearly, all cross sections have been normalized to their common average. This average drops exponentially with collision energy (cf. fig. 2), it can be fitted between 0.25 and 2.0 eV with less than 5% error to $\sigma_c = 61.8 \exp(-1.669E)$, where the units are eV and \AA^2 . One sees a large isotope effect for energies above ≈ 0.1 eV, or $1/50$ of the well depth, even if one includes only the natural isotopes. Comparison with fig. 2 reveals that the isotope effect becomes appreciable at the same energies, where the complex formation cross section drops markedly below the capture cross section. Fig. 1 shows further that the complex formation for asymmetric target is generally more probable than that for homonuclear target molecules.

To investigate this further, the calculations of set 2 were done. The results are tabulated in tables 1–3. The values are given in relative units, first with respect to the mass combination $m_A, 2, 2$ in order to show the dependence on target asymmetry, then the value for $m_A, 2, 2$ is given relative to $2, 2, 2$. The cross sections for this mass combination (identical to that for $1, 1, 1$!) are given in the

table captions. The tables demonstrate that the dependence of σ_c on the diatom masses is linear in the mass asymmetry parameter δ , i.e.

$$\sigma_c(m_A, m_B, m_C) = \sigma_c(m_A, 2, 2)(1 + a\delta). \quad (9)$$

This means linearity in the distance between the center of mass and the midpoint of the molecule, or in the torque produced by that lever and the target-projectile force. Ref. [1] has already predicted such a linear dependence, albeit with an energy independent coefficient. We presume that the source of this deviation lies in the erroneous assumption of identical transmission coefficients for all mass combinations in ref. [1].

To show the dependence of σ_c on the projectile mass, one has to introduce a second dimensionless mass parameter. After some experimentation we took Mahan's parameter f defined above. The results for $E = 1.0$ eV, $E_i = 0$ are displayed in fig. 3. One notes that the dependence on f is roughly linear. We interpret this as telling that the energy, which is lost on the first binary encounter between the projectile and one target atom, is decisive for the probability of forming a long-lived complex. Those encounters which do not store enough energy in degrees of freedom different from that of reactant translation, will produce a direct collision

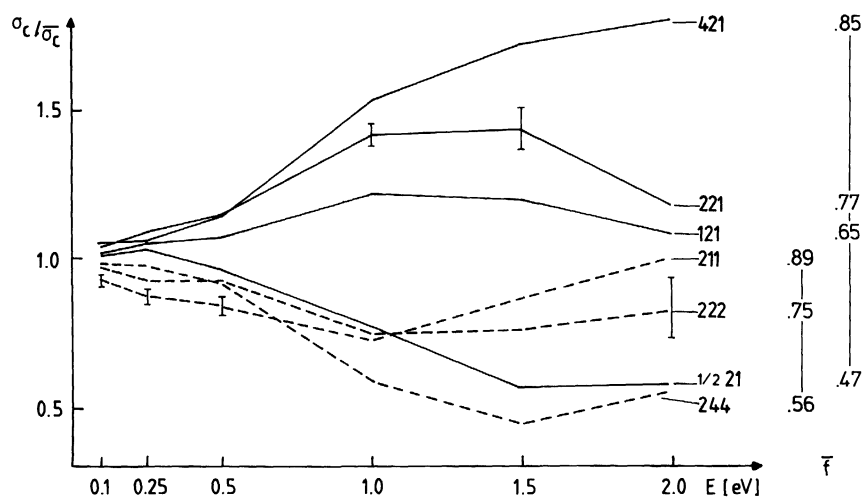


Fig. 1. Isotope effect of the complex formation cross section versus collision energy E . No internal energy of the target. The cross sections are normalized to their average value, which decreases exponentially with E as explained in the text. The masses are given as m_A, m_B, m_C where m_A is the projectile. The right margin shows the f -values of eq. (8).

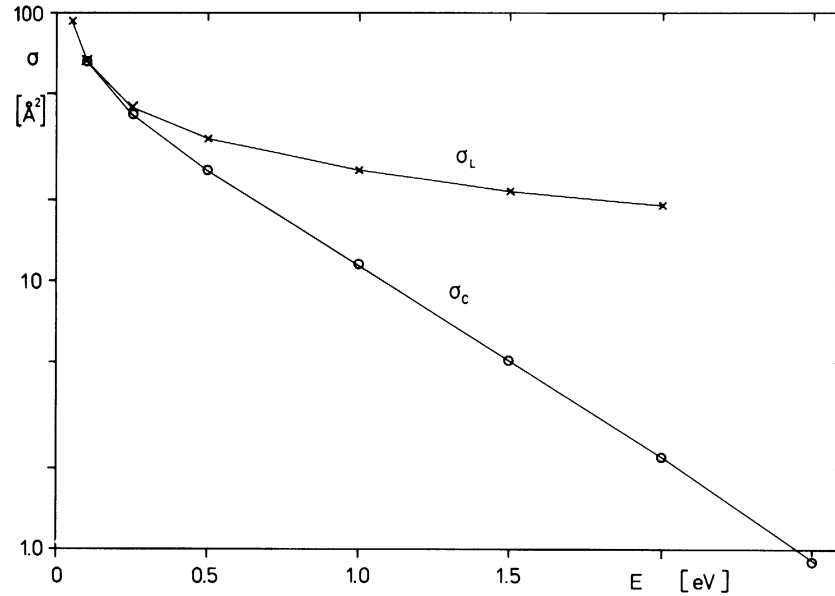


Fig. 2. Capture cross section, σ_L , and complex formation cross section, σ_c , for the $H^+ + H_2$ system. σ_L has been plotted for vanishing moment of inertia of BC (cf. eq. (6b)), while σ_c is the average over the mass combinations of fig. 1.

with generally only 2 or 3 minimum exchanges. At $E = 0.5$ eV (fig. 4) the linearity is broken for heavy targets. We interpret this as the transition from an impulsive regime, as presupposed by Mahan's formula, to a more adiabatic regime. Such an effect should be more prominent for large projectile

Table 1

Complex formation cross section σ_c at collision energy $E = 1.0$ eV, target energy $E_i = 0$, for masses m_A (projectile), and m_B , m_C (target). The last column gives $\sigma_c(m_A, 2, 2)$ relative to $\sigma_c(2, 2, 2) = 8.84 \text{ Å}^2$, while columns 2 to 5 show $\sigma_c(m_A, m_B, m_C)$ relative to $\sigma_c(m_A, 2, 2)$. The last line but one displays the average dependence on target masses, which can be fitted to a linear function of the mass asymmetry δ (see text). The last line shows the fitted values with fit parameter (cf. eq. (9)) $a = 5.0$

m_A	m_B, m_C				
	2, 2	1.8, 1.2	2, 1	3, 1	2, 2
4	1.00	1.72	2.10	2.56	0.96
2	1.00	1.35	1.88	2.40	1.00
1	1.00	1.23	1.85	2.38	0.88
0.5	1.00	1.16	1.47	1.90	0.70
average	1.00	1.36	1.83	2.25	
fit	1.00	1.50	1.83	2.25	

Table 2

Same as table 1 with $E = 0.5$ eV, $E_i = 0$. The reference cross section is $\sigma_c(2, 2, 2) = 24.4 \text{ Å}^2$, the fit parameter $a = 1.945$

m_A	m_B, m_C				
	2, 2	1.8, 1.2	2, 1	3, 1	2, 2
4	1.00	1.13	1.33	1.54	0.91
2	1.00	1.07	1.22	1.37	1.00
1	1.00	1.14	1.27	1.40	0.91
0.5	1.00	1.27	1.49	1.68	0.69
average	1.00	1.15	1.33	1.50	
fit	1.00	1.19	1.32	1.49	

Table 3

Same as table 1 but for $E = 0.5$ eV, $v = 2$, $j = 0$, corresponding to internal energies between 0.93 eV (2, 2), and 1.13 eV (2, 1). The reference cross section for this table is $\sigma_c(2, 2, 2) = 20.0 \text{ Å}^2$, the fit parameter $a = 1.637$

m_A	m_B, m_C				
	2, 2	1.8, 1.2	2, 1	3, 1	2, 2
4	1.00	1.16	1.33	1.49	0.96
2	1.00	1.12	1.24	1.42	1.00
1	1.00	1.10	1.24	1.38	0.98
0.5	1.00	1.22	1.32	1.36	0.82
average	1.00	1.15	1.28	1.41	
fit	1.00	1.16	1.27	1.41	

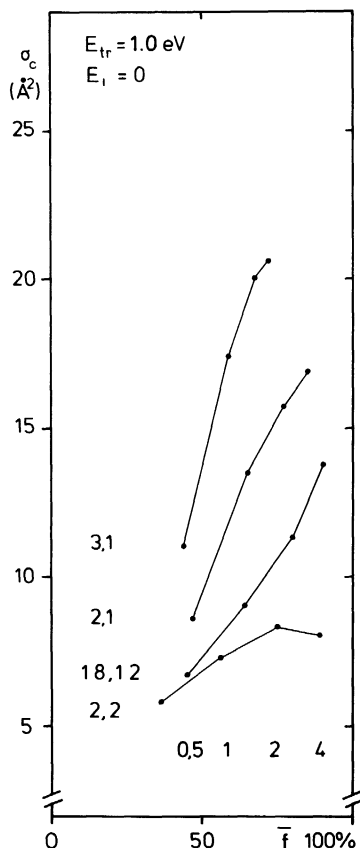


Fig. 3. Complex formation cross sections as a function of projectile mass (bottom numbers), and target masses (left numbers) versus the Mahan parameter f of eq. (8) for $E = 1.0$ eV, $E_i = 0$.

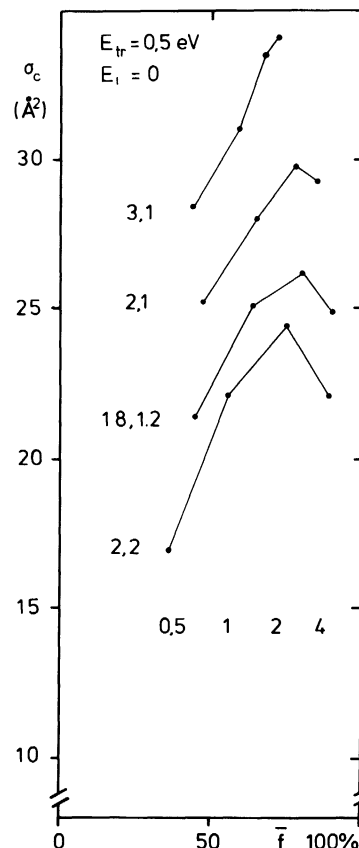


Fig. 4. Same as fig. 3 for $E = 0.5$ eV, $E_i = 0$.

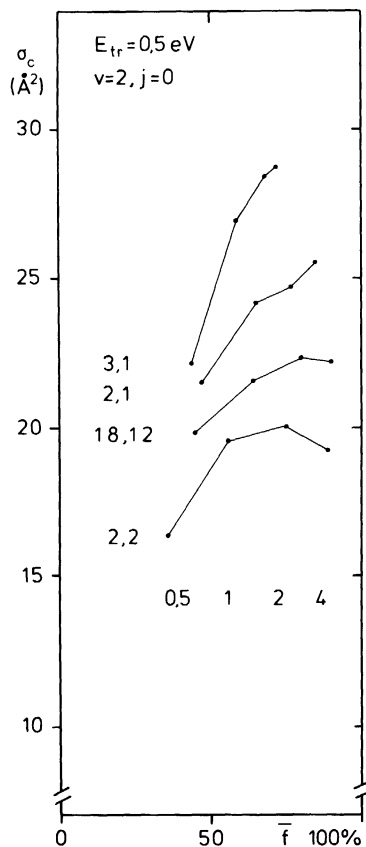
masses (low velocity of approach), and for low collision energy as it does.

The influence of vibrational excitation of the target can be seen comparing figs. 4 and 5. In fig. 5 the initial condition is $v = 2$, leaving about 1 eV of internal energy in the target. In accord with earlier observations [7] this decreases σ_c , but not too much. The mass dependence is also not much different from the case of zero internal energy. This is also true, if initial energy is supplied in the form of target rotation. Four computations with $E_{rot} \approx 1$ eV ($j \approx 16$) show an effect within 20% of that of vibration.

To show somewhat more detail of what happens, we provide fig. 6 (cf. also fig. 6 of ref. [7]). It

presents the complex formation probability as a function of impact parameter b (i.e. of total angular momentum J) for two mass combinations and two internal energies. One observes that the main difference between both mass combinations lies in the values of P_c for large impact parameters: P_c drops much earlier with b for the asymmetric target HD than for H_2 . Comparison of the panels for $E_i = 0$ and $v = 2$ shows again [7] that the effect of vibrational excitation is different from that of translational energy: it pushes $P_c(b)$ as a whole to values markedly below 100%.

The purpose of our last set of calculations was to find out how the relation $\sigma_c = \sigma_L$ (meaning that every captured trajectory is long-lived) is approached if the collision energy is more and more decreased. Calculations were done for $E = 0.05$

Fig. 5. Same as figs. 3 and 4 for $E = 0.5$ eV but $v = 2$.

and 0.02 eV with a reduced set of mass combinations to compensate for the longer computing times involved. The results are presented in tables 4 and 5.

At 0.05 eV there is still some isotope effect. The values of σ_c for initial condition $E_i = 0$ are ordered like those at 0.1 and 0.25 eV, the relative spread from 2, 2, 1 to 2, 2, 2 now being 2.4% instead of 7.3 and 16.3%. The difference between the capture and the complex formation cross sections, which we call the direct cross section, σ_d , is now difficult to assess, since eq. (4) gives only a *nominal* value of σ_L . But the following argument allows us at least to give a lower limit to this difference: Any trajectory which makes at least one minimum exchange must (at these low energies) have overcome the centrifugal barrier, which is at $R = 4.1$ Å for $E = 0.05$ eV. So the cross section of trajectories with 1 to 7 minimum exchanges may be regarded as a lower limit to the true direct cross section. (As an aside we may say that trajectories with only 1 minimum exchange have never been found.) It is a lower limit only, since it is conceivable that a very slow projectile surmounts the centrifugal barrier at one point, but is then "overtaken" by the rotation of the non-spherical barrier, and repelled by another, higher part of it without making a minimum exchange.

Tables 4 and 5 show that σ_d vanishes near

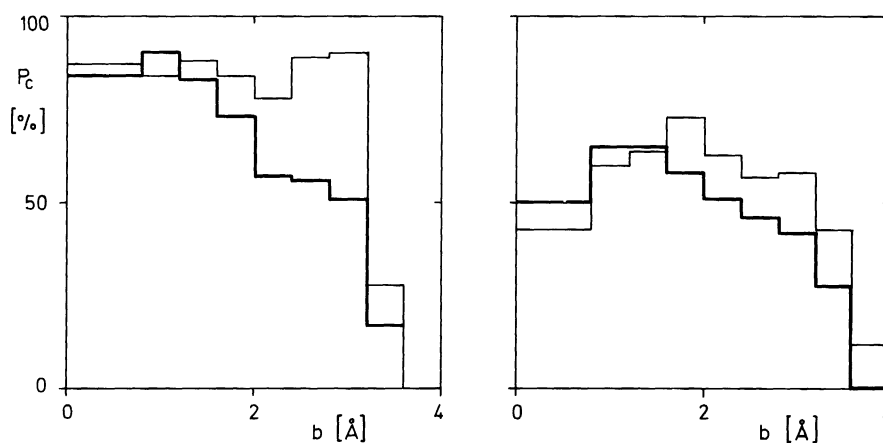


Fig. 6. Complex formation probability P_c versus impact parameter b . P_c has been computed for bins 0.4 Å wide, except for the first one, which is twice that wide. The collision energy is 0.5 eV, the internal energy is zero in the left panel, and corresponds to $v = 2$ in the right one. Thin lines: masses 2, 1, 1; thick lines: masses 2, 2, 1.

Table 4

Cross sections (in \AA^2) for selected mass combinations and target energies at a collision energy of 0.05 eV. σ_c : complex formation, σ_d : direct collisions (1 to 7 minimum exchanges), σ_L : nominal capture cross section (eqs. (4)–(5))

Masses	v, j	E_t	σ_c	σ_d	$\sigma_c + \sigma_d$	σ_L
2, 2, 1	–1/2, 0	0.00	94.6	0.1	94.7	95.3
	0, 0	0.24	93.4	1.9	95.3	
1, 2, 1	–1/2, 0	0.00	93.6	0.3	94.0	96.3
	0, 0	0.24	89.9	4.7	94.6	
	1, 0	0.69	83.2	12.6	95.8	
	2, 0	1.13	76.6	20.7	97.3	
	–1/2, 15	1.31	72.6	21.3	93.9	
2, 2, 2	–1/2, 0	0.00	92.4	0.6	93.0	95.9
	0, 0	0.20	87.7	5.3	93.0	
1, 2, 2	–1/2, 0	0.00	92.7	0.0	92.7	97.4
	0, 0	0.20	89.0	4.0	93.0	
	1, 0	0.57	83.1	10.9	94.0	
	2, 0	0.93	73.4	20.4	93.8	
	–1/2, 17	0.95	71.8	23.1	94.9	
typical error			± 1.5	± 0.7	± 1.3	

$E = 0.05$ eV (which is as low as 1/100 of the well depth!), if the initial state has no internal energy. If this is not the case, σ_d is finite even at $E = 0.02$ eV, and probably for any lower energy of collision. σ_c is an almost linearly decreasing function of the target's initial energy, and it makes barely any difference whether this is supplied as vibra-

tion or as rotation. The derivative $\partial\sigma_c/\partial E_t$ is again mass dependent, in the only case where we can compare we find that the relative derivative $(1/\sigma_c) \partial\sigma_c/\partial E_t$ is almost the same for $E = 0.05$ and 0.02 eV.

This behaviour induces a new type of isotope effect if one runs the calculation as a quasiclassi-

Table 5

Selected cross sections as in table 4 for a collision energy of 0.02 eV

Masses	v, j	E_t	σ_c	σ_d	$\sigma_c + \sigma_d$	σ_L
2, 2, 1	–1/2, 0	0.00	135.8	0.0	135.8	135.0
	0, 0	0.24	132.5	3.5	136.1	
1, 2, 1	–1/2, 0	0.00	135.3	0.0	135.3	135.8
	0, 0	0.24	131.0	4.5	135.5	
2, 2, 2	–1/2, 0	0.00	134.2	0.0	134.2	135.5
	0, 0	0.20	128.4	6.2	134.5	
1, 2, 2	–1/2, 0	0.00	133.8	0.0	133.8	136.7
	0, 0	0.20	129.2	5.0	134.2	
	1, 0	0.57	119.3	14.9	134.2	
	2, 0	0.93	108.5	25.7	134.2	
	–1/2, 7	0.20	131.0	2.8	133.8	
	–1/2, 17	0.95	106.4	27.8	134.2	
typical error			± 1.9	± 1.0	± 1.6	

cal one, i.e. includes the target's zero-point energy in the initial conditions. Table 4 shows this for $E = 0.05$ eV. The spread between the largest and the smallest of the four cross sections has now increased from 2.4 to 6.5%. The order of the cross sections has remained the same, but this is in part fortuitous, since σ_c depends now on the absolute mass scale. One sees, in addition, that this type of isotope effect is appreciable only for hydrogen compounds, where zero-point energies are likely which are more than a vanishing fraction of the well depth.

5. Concluding discussion

We have calculated in this paper complex formation cross sections in a typical triatomic potential well, which has no non-rotational barrier. We define a collision complex as long-lived if its decay is independent from its origin, save for conserved quantities. Classical calculations done for a variety of mass combinations and initial conditions show:

(1) For medium collision energies (in proportion to the well depth) the complex formation cross section is only a fraction of the capture cross section, and it is strongly mass dependent.

(2) The mechanism leading to the "trapping" of the projectile in the form of a long-lived complex, is the storage of translational collision energy in internal vibrations of the complex. The effectiveness of this storage depends very much on the masses involved.

(3) As a rule, asymmetric target molecules lead more often to complex formation than symmetric ones, because an early energy transfer into target rotation takes place. (This energy is later also transferred into vibration.)

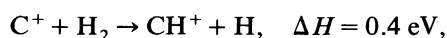
(4) For low energies approaching 1/100 of the well depth the direct collision cross section vanishes, i.e. the complex formation cross section approaches the capture cross section, *if* the target contains no internal energy.

(5) Target excitation prevents the identity of capture and complex formation even for the lowest collision energies.

(6) The dependence of σ_c on internal excitation

leads to another kind of isotope effect, induced by the zero point motion of the target. This effect will be noticeable mainly for hydrogen compounds.

Our results are by no means restricted to the H_3^+ potential, which we have used for the calculations. The scaling properties of the (classical) equations of motion make the results valid independent of the potential's well depth, or its extension. Only different potential *shapes* may lead to different behaviour. An example is the reaction



which shows a large isotope effect not yet understood [4,5]. It is of the same order of magnitude as the effects discussed here, but does not quantitatively fit to our results. This, however, is no wonder in view of the very different potential situation for CH_2^+ involving avoided crossings and the like.

The crucial question, whether our results will remain valid in the quantum world, cannot today be answered precisely, since quantum calculations in three dimensions are still unfeasible. From our general knowledge on the limits of the classical trajectory method we feel that the picture, which we painted, will not change too much. Especially we want to conjecture that the low-energy results, e.g., that target excitation prevents complex formation to a certain degree even at the lowest collision energies, remain valid. To see this one has only to imagine a wave packet as a Wigner-distributed bundle of trajectories: its behaviour is predictable from our results. In a different language one can also say the following: In the quantum system the scattering from a deep well will, of course, be dominated by resonances, which the classical computation does not include. However, it is the *average* resonance behaviour, which determines the main features of complex formation and decay in the quantum system. There is no reason why this average behaviour should not be simulated reasonably well by the classical calculation.

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References

- [1] F.S. Klein and L. Friedman, J. Chem. Phys. 41 (1964) 1789.
- [2] F.S. Klein, Ann. Rev. Phys. Chem. 26 (1975) 191.
- [3] P.M. Hierl, J. Chem. Phys. 67 (1977) 4665.
- [4] K.M. Ervin and P.B. Armentrout, J. Chem. Phys. 84 (1986) 6750.
- [5] P.F. Fenelly, Ph.D. Thesis, Brandeis University (1972); D. Cahnbley, Diplomarbeit, Freiburg University (1982); K.M. Ervin and P.B. Armentrout, J. Chem. Phys. 84 (1986) 6738.
- [6] W.H. Miller, J. Chem. Phys. 52 (1970) 543.
- [7] D. Gerlich, U. Nowotny, Ch. Schlier and E. Teloy, Chem. Phys. 47 (1980) 245.
- [8] Ch.G. Schlier, in: Energy storage and redistribution in molecules, ed. J. Hinze (Plenum Press, New York, 1983) p. 585.
- [9] O. Brass and Ch. Schlier, to be published.
- [10] K. Kern and Ch. Schlier, Z. Physik D 1 (1986) 391.
- [11] W.J. Chesnavich, T. Su and M. Bowers, J. Chem. Phys. 72 (1980) 2641; W.J. Chesnavich, J. Chem. Phys. 77 (1982) 2988.
- [12] K. Rynefors and S. Nordholm, Chem. Phys. 95 (1985) 345.
- [13] E. Pollak, J. Chem. Phys. 86 (1987) 1645.
- [14] B.H. Mahan, J. Chem. Phys. 52 (1970) 5221, eq. (1); J. Chem. Educ. 41 (1974) 308, eq. (13).