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In 1984, Schelling and Castleman discussed whether the lifetime of a complex formed in an ion-molecule reaction might depend on the anisotropy of the ion-molecule potential. Their model was that of a rigid rotor with spherical repulsion, but anisotropic polarizability. In this paper, we contend that models employing a rigid diatom are quite unrealistic to discuss complex lifetime, since the latter is predominantly determined by intermediate energy storage into vibration. We use, instead, a model system with three pair potentials of the Morse type and vary the equilibrium distances to generate different anisotropies of the potential. Trajectory calculations show a definite influence of this parameter both on the complex formation cross section and on lifetime. These lifetimes are one order of magnitude longer than those computed with the rigid diatom model, after the calculations have been scaled to the same masses and potential parameters. The lifetimes turn out to be roughly proportional to the period of the fastest normal mode of the intermediate molecule, and their behavior is generally in accord with RRKM theory.

I. INTRODUCTION

The duration of an atom-diatom collision process, i.e., the lifetime of the triatomic intermediate, is an important property of this process. In particular, it determines the efficiency of many secondary processes, be it intramolecular energy transfer, or weak coupling to a second potential energy surface, or any process involving a third body collision. As an example, it has been proposed^{1,2} that the increased rate of charge-transfer in the reaction $\text{N}_2\text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2\text{O}$, if the N_2O^+ is vibrationally excited, is due to a longer lifetime of the N_3O_2^+ complex. Similarly, expressions for the rate of vibrational quenching or three-body association have been written down, in which the complex formation rate times the complex lifetime plays the key role.² It is, therefore, an interesting question how the complex formation cross section σ_c and the lifetime τ of the triatomic complex depend on the parameters of the collision, especially on the shape of the potential energy surface.

The problem how σ_c and τ depend on the energies involved in the collision (E_{trans} : translational, E_{vib} : vibrational, and E_{rot} : rotational) has been addressed by our group in former papers,³⁻⁵ in which the DIM potential for H_3^+ has been used as a typical model potential. We have also looked for kinetic isotope effects, which are quite large in that energy regime where σ_c becomes smaller than σ_L , the capture or "Langevin" cross section.⁵ The influence of the mass ratios on lifetime is small.⁴ However, τ is heavily dependent on the total angular momentum,⁶ a property which is generally lost by the necessary integration over all such momenta.

These results are not at all limited to collisions of $\text{H}^+ + \text{H}_2$ and its isotopic variants, since the scaling behavior of σ_c and τ can readily be deduced. In classical mechanics, which we always employ (and must employ, since quantum calculations are still unfeasible), one has

$$\sigma_c = \pi r_0^2 \cdot fct_1 \left(\frac{m_k}{m}, \frac{E_k}{E}, \frac{E}{V_0} \right), \quad (1)$$

$$\tau = r_0 \cdot \left(\frac{m}{V_0} \right)^{1/2} \cdot fct_2 \left(\frac{m_k}{m}, \frac{E_k}{E}, \frac{E}{V_0} \right). \quad (2)$$

Here, m_k ($k = 1, \dots, 3$) are the participating masses, $m = \sum m_k$ the total mass, E_k ($k = \text{trans, vib, rot}$) the energies, $E = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}}$ the total energy, V_0 a typical potential energy, e.g., the well depth, r_0 a typical potential distance, and fct some function of the dimensionless parameters which it has as arguments. Parameters not written down include the shape parameters of the potential energy surface and the total angular momentum (in the combination $J^2/mr_0^2V_0$) which is seldom specified in an experiment. We discuss this aspect in full breadth, because this scaling behavior allows us to draw order-of-magnitude conclusions for systems quite different from $\text{H}^+ + \text{H}_2$, e.g., $\text{Na}^+ + \text{N}_2$ (or $\text{Ar} + \text{Ar}_2$ for that matter). Implicit in the use of such scaling for quite different systems is the assumption that the potential shape parameters neglected in writing Eqs. (1) and (2) do not appreciably change σ_c and τ , say, by not more than half an order of magnitude.

A systematic investigation how σ_c and τ depend on potential shapes has not yet been performed. Two papers by Davies⁷ are in loose correspondence to the problem, while Schelling and Castleman⁸ address this question explicitly. The latter paper was the incentive for our investigation, since we believe that their model is quite unrealistic in using a rigid diatom with an anisotropic long-range potential to determine the complex lifetime. This restriction prevents the intermediate storage of energy in vibration, which, on the other hand, is the main mechanism producing long-lived (as contrasted to direct) molecular collisions, as is quite well known.⁹ Thus, the lifetimes computed in Ref. 8 are more than one order of magnitude too small.

Indeed, neglecting the influence of potential shape, we may scale our results on $\text{H}^+ + \text{H}_2$ and its isotopes⁴ to their system $\text{Na}^+ + \text{N}_2$. Taking r_0 in Eq. (1) as the equilibrium distance (2.15 instead of 0.92 Å), V_0 as the well depth (0.537

instead of 4.92 eV), and m as total mass (51 instead of 3 or 4) and utilizing the scaled arguments to derive the value of $fc t_2$, we arrive at about 40 ps for the lifetime of the $\text{Na}^+ \text{N}_2$ complex at the given total energy of 59 meV. This estimate has an error of perhaps a factor of 3. It is about 25 times larger than the lifetime of Ref. 8, and seems much more reasonable in view of the three-body association data cited there, since a stabilization efficiency of 1.0 for He, which is assumed in Refs. 2 and 8, is certainly not what one expects.

In this situation the question arises how a more realistic calculation could be done, which shows the influence of potential anisotropy, or, more generally, of potential shape on the complex formation rate and on complex lifetime. Actually, an anisotropy of only the long range potential is not what we are looking for. Its influence on the capture cross section, which at low energy determines the complex formation, is generally small.¹⁰ [Note that the results of Ref. 10 obtained in two dimensions (2D) must be "diluted" when used in 3D, since the potential has still axial symmetry, a remark which is also valid for the calculations of Ref. 8.]

Another bit of information comes from our calculations with the H_3^+ potential and asymmetric diatom masses (e.g., $\text{H}^+ + \text{HD}$).⁵ We found that in the collision energy range above a few percent of the well depth (where complex formation becomes more and more improbable relative to capture) large isotope effects exist for σ_c , but not for τ . The former can to a large extent be traced to the additional torque on the diatom originating from the difference of center-of-mass and center-of-force in such systems, i.e., to an additional anisotropic long-range force. This additional force has, however, only a small influence on the lifetime, which is mediated by the angular momentum constraints involved. These effects prolong the "normal," vibrationally determined lifetimes of the triatomic complexes in the same way as the effects seen by Schelling and Castleman⁸ prolong an otherwise direct collision. Averaged over all angular momenta they are not big: the largest effect which we saw, the lifetime ratio for masses 1.2.2 compared to 2.1.2, was only a factor of 1.6.

So, in order to see real effects of the potential shape, we decided to do a calculation in which the overall shape of the potential is varied by changing its equilibrium geometry while the other parameters are kept constant. In Sec. II we will discuss this choice further and show the results. A final discussion follows in Sec. III.

II. COMPUTATIONS AND RESULTS

Trajectory calculations of complex lifetimes are very time consuming, since one has not only to compute very long trajectories, but these are, in addition, very unstable. So one must decrease the integration stepsize the more the longer one integrates. In this study we wanted, therefore, to change only *one* geometry parameter of the potential. The well depth, on which the lifetime reacts so sensitively had, of course, to be kept constant. To simplify the calculation we took the triple-Morse ansatz:

$$V(R_1, R_2, R_3) = \sum_i^3 V_i(R_i), \quad (3a)$$

$$V_i = D_i \left\{ \left(1 - \exp \alpha_i \frac{R_{ei} - R}{R_{ei}} \right)^2 - 1 \right\}. \quad (3b)$$

Our reference potential is a crude fit of this potential shape to the H_3^+ well with $D_i = 3.2232$ eV, $\alpha_i = 1.437 \text{ \AA}^{-1}$, and $R_{ei} = 0.91765 \text{ \AA}$, $i = 1, \dots, 3$. This potential was altered by breaking the D_{3h} symmetry into C_{2v} , setting $R_{e1} = R_{e3} = a \cdot R_{e2} = a \cdot 0.91765 \text{ \AA}$. All D_i and α_i were kept constant. a is therefore the only potential parameter which is varied in our calculations. Further initial conditions were $E_{\text{trans}} = 0.5$ or 0.25 eV, $E_{\text{vib}} = E_{\text{rot}} = 0$, while the remaining variables were Monte Carlo sampled.

The complex formation cross section σ_c was defined as before^{3,5} by the requirement of at least eight minimum exchanges on the trajectory. As a minimum exchange we had defined the change of the identity of the smallest internuclear distance, i.e., of $R_{\min} = \min(R_1, R_2, R_3)$. Two minimum exchanges can approximately be identified with one inner turning point of the actual $R_{\min}$, or with one molecular "vibration." To extend this definition to cases where the equilibrium distances R_{ei} are different, we must now use scaled distances. That is, we define $\rho_i = R_i/R_{ei}$ and $\rho_{\min} = \min(\rho_1, \rho_2, \rho_3)$ and count the changes of the identity of $\rho_{\min}$. Apart from this change, the computation of lifetimes proceeded as before.⁴ For each computation 1000 or 2000 trajectories were started and stopped when finished or when a certain time limit was reached, which was taken between 800 fs ($a \leq 1$) and 2000 fs ($a = 3$). The number of "living" complexes was then fitted to an exponential decay law. The stated errors are partially a consequence of small deviations from this law, which could be traced as before^{4,6} to the dependence of τ on total angular momentum J . Our results are, therefore, average lifetimes, weighted with the probability $P(J)$ that a complex is formed if a trajectory is started with some J as the initial value. We remark that our definition of lifetime is completely independent of the details of the definition of a "long-lived" complex.

The results are presented in Table I and in Figs. 1 and 2. Both cross sections and lifetimes depend markedly on the

TABLE I. Complex formation cross sections σ and lifetimes τ as a function of geometry parameter a for two collision energies.

a	$E = 0.25$ eV		$E = 0.50$ eV	
	σ ($\text{\AA}^2$)	τ (fs)	σ ($\text{\AA}^2$)	τ (fs)
0.5	18.8	2760	13.7	730
0.6	25.8		19.4	
0.7	34.0		23.8	1030
0.8	44.3	4830	28.5	1260
0.9	53.7		31.6	1530
1.0	60.2	6020	29.5	1780
1.2	64.5		29.1	1610
1.5	83.4	6650	32.9	1560
2.0	137	6780	42.8	1520
2.5	205		49.5	
3.0	219	6630	50.3	1860
Typ. error	3%	6%	4%	4%

FIG. 1. Complex formation cross section vs asymmetry parameter a . The collision energy is 0.5 eV (upper curve, left scale) and 0.25 eV (lower curve, right scale). The statistical errors are indicated where necessary. The fits are explained in the text.

shape of the potential, but by no means as strongly as on energy, where the dependence is exponential. For both properties, the equilateral triangle ($a = 1$) seems to be a distinct borderline between the region $0.5 \leq a \leq 1$, where σ_c and τ depend steeply, but linearly on a , and the region $a \geq 1$ where the increase of σ is slower and τ becomes almost constant. Two properties of the molecule have a singular value at $a = 1$: (i) The second (A_1) and third (B_1) normal vibrations of the molecule become degenerate. (ii) Two moments of inertia become equal, and the moment with respect to the C_2 axis changes from unstable (I_{bb}) to stable (I_{aa}).

Let us first discuss the cross sections: Their increase with a is actually expected since the "size" of the potential well is increasing with a . Another parameter which perhaps describes better the aspect of this size is the area A of the triangle formed by the three equilibrium distances R_{ei} ($i = 1, \dots, 3$), which is (in units of R_{e2}^2)

$$A = (a^2 - 1/4)^{1/2} \simeq a - 1/8a - \dots \quad (4)$$

At $E = 0.25$ eV linear fits of $\sigma(a)$ and of $\sigma(A)$ are both quite good ($r = 0.991$ and 0.983 , respectively), while at $E = 0.5$ eV the fit of σ vs A is somewhat better, and the best fit we found (shown in Fig. 1) is

$$\sigma = 30.0 \cdot A^{0.415} \quad (5)$$

FIG. 2. Complex lifetime vs asymmetry parameter a : + : collision energy 0.5 eV. $\times$: collision energy 0.25 eV. The lifetimes for 0.25 eV have been divided by the factor 3.717 [from Eq. (6)] to bring them on the same scale. The thin line is $155 \cdot \tau_0$, where τ_0 is the period of the fastest normal vibration of the complex (cf. also the text).

In view of Table I it is not worthwhile to explicitly give the other fits here. We feel that the general trend of $\sigma(a)$ is well explained by this effect of size. A look on the capture cross section for $E = 0.5$ eV (defined here for simplicity as the cross section for those trajectories, which make at least one minimum exchange) shows that it increases somewhat more than linearly with a . The slow increase of σ_c for $a > 0.9$ is therefore due to a decrease of the complex formation probability, i.e., the percentage of captured trajectories making more than seven minimum exchanges. This can be traced to an increasing probability for these trajectories to make a *direct reactive* collision. In addition to this general trend there is a wavy deviation near $a = 1$, which we rationalize with the special situation of the equilateral triangle mentioned above.

The more important property for this paper is the lifetime of the complexes. In Fig. 2 we show $\tau(a)$ for $E = 0.5$ eV directly, while the lifetimes for $E = 0.25$ eV are divided by 3.717. This is the scaling factor expected from the RRKM-type formula

$$\tau = \tau_0 \cdot \left(\frac{D + E}{E} \right)^s \quad (6)$$

where D is the well depth as seen from the asymptotic channel (6.4464 eV $= 2 \cdot D_i$ in our case), E is the energy available for the dissociation of the complex, and the expected expo-

nent s is 2. One observes that these scaled values fit very well to those for $E = 0.5$ eV. This can also be expressed by calculating a value of s from each pair of lifetimes at a given a . These s average to 2.06 ± 0.16 , i.e., within errors to the expected value.

In Fig. 2 we show also the curve $\tau = 155 \cdot \tau_1$, where τ_1 is the period of the fastest of the three normal vibrations of our H_3^+ model. For $a \leq 0.65$ this is the asymmetric B_1 mode, while for $a \geq 0.65$ it is the symmetric stretch (A_1). The frequencies of all modes were computed from the eigenvalues of the Jacobi determinant. The fit of this curve to the average dependence of the lifetimes on a is very good. If one computes τ_0 of Eq. (6) from this curve one finds $\tau_0 = 0.80 \cdot \tau_1$. From the theory of unimolecular decay⁹ one has on the other hand

$$k_{\text{uni}} = \frac{1}{\tau_0} = \sum_i^3 \frac{W_i^\dagger}{h\rho}, \quad (7a)$$

where $W_i^\dagger$ is the number of states at an energy E at the i th transition state ($i = 1, \dots, 3$), and ρ the density of states of the excited molecule at this energy. In the usual harmonic oscillator approximation⁹ this is evaluated to

$$W_i^\dagger = \frac{E^2}{h^2 \nu_{2i}^\dagger \nu_{3i}^\dagger} \quad (7b)$$

and

$$\rho = \frac{(E + D)^2}{h^3 \nu_1 \nu_2 \nu_3}. \quad (7c)$$

(Here ν_i , $i = 1, \dots, 3$ are the frequencies of the complex, while the two frequencies $\nu_k^\dagger$ of the transition state have been numbered 2 and 3, D enters because the energies must be referred to a common zero.) This leads to

$$k_{\text{uni}} = \frac{1}{\tau} = \frac{1}{\tau_0} \left(\frac{E}{E + D} \right)^2 = \left(\frac{E}{E + D} \right)^2 \cdot \sum_i^3 \frac{\nu_1 \nu_2 \nu_3}{\nu_{2i}^\dagger \nu_{3i}^\dagger} \\ = \left(\frac{E}{E + D} \right)^2 \cdot 3\nu_1 \cdot \left\langle \frac{\nu_2 \nu_3}{\nu_2^\dagger \nu_3^\dagger} \right\rangle_{\text{av}}. \quad (7d)$$

We can now identify ν_1 with the fastest mode of the complex, and extract a value of 0.42 for the average of $(\nu_2 \nu_3) / (\nu_2^\dagger \nu_3^\dagger)$, which is not unreasonable in view of the approximations made.

As a further result we present in Fig. 3 the fraction P_{nr} of those complexes which decay into the nonreactive channel. For $a = 1$ its value agrees within errors with the expected one-third, but it is much larger for $a \ll 1$ and much smaller for $a \gg 1$. We also show P_{nr} for those trajectories which have experienced at least 2 or at least 20 minimum exchanges. The appreciable difference which exists for large a (only) between 8 and 20 minimum exchanges indicates that eight minimum exchanges are barely enough for the complex to loose its "memory" if $a \gg 1$. In general, the behavior of P_{nr} suggests a correlation of the preferred decay channel with the nuclear motion of the complex in the sense that the fastest moving atom is that which preferentially dissociates off. This can also be expressed by saying that the channel with the slowest motions is the preferred transition state, which is what one expects from theory.

FIG. 3. Fraction of nonreactive scattering as a function of the asymmetry parameter a . The curves marked with numbers M consider only completed trajectories with more than M minimum exchanges. Typical statistical errors are shown.

III. GENERAL DISCUSSION

For a simple potential ansatz, which permits different shapes of the potential well, we have calculated complex formation cross sections and complex lifetimes as a function of an asymmetry parameter a . The general trend of the cross section can be understood from the change of the size of the potential, while that of the lifetimes is highly correlated with the fastest vibrational mode of the complex. Small additional effects seem to be connected with the special D_{3h} symmetry which the potential assumes for $a = 1$. On an absolute scale the lifetimes from this paper are similar to those computed earlier for H_3^+ and its isotopes with a more realistic potential (see Fig. 2 of Ref. 4) and consistent with what one expects from RRKM and other statistical theories.

The effects computed by Schelling and Castleman with an anisotropic rigid-rod model⁸ do exist, and have actually been also observed by Dugan.¹¹ He used a potential which modeled an ion plus a polarizable dipole with hard core. The average lifetimes computed in Ref. 8 are between 1 and 2.5 ps, those of Ref. 11 between 4 and 30 ps, and thus similar to our values. A comparison would, however, be totally pointless without taking the parameter differences into account. We can do this by joining Eqs. (2) and (6) to form the specialized scaling equation (neglecting the very slight dependence of τ on m_k/m , and noting that τ does actually not depend on E_k/E)

$$\tau = c \cdot r_0 \left(\frac{m}{D} \right)^{1/2} \cdot \left(\frac{E}{E + D} \right)^{-2}, \quad (8)$$

where c is a constant, and V_0 has been identified with D . Using the data mentioned in Sec. I we arrive at a scaling factor of 18 with respect to the first example (Na^+N_2) of Ref. 8, which means that we have to compare a lifetime of the order of 25 ps with the 1.5 ps of Ref. 8. This shows that the inclusion of the vibrational degrees of freedom is *essential*, if one wants to make a realistic model of a long-lived molecular complex. The dynamical reason for this becomes clear from an examination of a series of plots of complex trajectories: the typical motion of the triatomic complex is *vibration* involving all three atoms equally, and *not* the hindered rotation of a diatom with respect to the third atom. This view is also supported by the statistical theory of unimolecular decay (even if it is doubtful whether it can be applied to the rigid rotor case): Making the diatom rigid will reduce the power of $\{E/(E + D)\}$ in Eq. (6) from 2 to 1, which decreases τ by an order of magnitude at the energy involved.

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