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The classical Rice–Ramsperger–Kassel–Marcus formula is tested at an accuracy level of a few percent by comparing results of numerical phase space integration with lifetimes deduced from trajectory calculations. The test object is HD_2^+ ; the calculation has been done for total energies of 0.5, 1.0, and 1.5 eV above dissociation, and for total angular momenta of 0–60 $\hbar$. Presupposing that the trajectory calculations show the true classical dynamics, we find systematic deviations of up to 40% of the RRKM results. They can be fully explained by the influence of “direct trajectories,” a special kind of nonergodic behavior of the system. After correction for this phenomenon, both methods agree to within the accuracy of the calculations, which is about 3%. We also verified that the discrepancy vanishes when the energy approaches the dissociation energy.

I. INTRODUCTION

The Rice–Ramsperger–Kassel–Marcus (RRKM) formula for the rate of unimolecular decomposition of a molecule^{1–5}

$$k(E, J) = \frac{N^\ddagger(E, J)}{h\rho(E, J)} \quad (1)$$

is probably the most ubiquitous statistical formula in molecular reaction dynamics. Here, $N^\ddagger$ is the number of states below the energy E “at the transition state,” i.e., for a fictitious molecule derived from the original one by fixing the reaction coordinate R at the transition state. ρ is the density of states at energy E of the “activated molecule,” whose phase space is closed by including only values of R smaller than $R^\ddagger$, the position of the transition state. In both cases, J must be fixed, and microcanonical ensembles must be used to calculate these numbers. Though not too many experiments exist in which the J -dependent, “specific” rate is measured, we will see that it is important for our discussion to compute this detail. As usual, our values for $N^\ddagger(E, J)$ and $\rho(E, J)$ do not contain the factor $2J+1$ from the M degeneracy, which drops out from the rate $k(E, J)$ anyhow.

The title question “How accurate is RRKM theory” can be asked and answered at many different levels of scope and accuracy. Several issues connected with this question have been discussed, e.g., in Refs. 5–8. In this paper, we will restrict the question and ask only how accurate the rate equation (1) is. Even then, it has many facets. Ideally, one would like to compare the predictions of RRKM theory with experiments in a way similar to a comparison of atomic theory with atomic spectra. However, there are many obstacles. Experiments are indirect (e.g., draw conclusions from the shape of a fall-off curve), measure only averaged quantities such as $k(E)$ or even $k(T)$, need fit parameters for the comparison, or are just imprecise (an agreement within a factor of 2 is generally considered “good”). On the other hand, formula (1) is generally evaluated with gross approximations and it is not obvious at all what a correct computation of $N^\ddagger(E, J)$ and $\rho(E, J)$ is.

RRKM theory, like its ancestor transition state theory, is intrinsically a classical theory. (Its premises can, e.g., be seen very clearly from the derivation in Nikitin’s book.⁹) The occurrence of Planck’s constant h in Eq. (1) is artificial, it stems from interpreting the numerator as a number of states instead of a phase space volume, and the denominator as a state density instead of a volume density. We can, of course, interpret it as a quantum formula, and this is justified by several quantum derivations of the same formula (cf. Refs. 10 and 11), which, however, must make assumptions completely different from their classical counterpart, since concepts like “point of no return” do not exist in quantum mechanics.

In a quantum interpretation, the first problem in evaluating Eq. (1) is the computation of the energies of all quantum states and resonances (!) making up $N^\ddagger(E, J)$ and $\rho(E, J)$. This is still an unfeasible computational task, and H_3^+ is the only exception,^{12–16} where at least for certain values of J all bound states have been calculated. Even here, the high- J states are barely converged and the resonances have not yet been done. As has been shown recently by the authors,^{17,18} the problem of calculating all the single states and resonances can be circumvented by computing the *averaged* functions $N^\ddagger(E, J)$ and $\rho(E, J)$ (the ones which are needed) *semiclassically* from a phase space integration, which includes corrections for zero point effects. This is feasible with today’s workstations for three-, four-, and, perhaps, five-atomic systems, and with some approximation also for larger ones (cf. Refs. 19–21).

A final obstacle, however, for a precise comparison of RRKM theory to experiments remains—the fact that, for most molecules, we are far from knowing their potential energy surface well enough to do an accurate calculation of state densities, particularly at energies approaching and above the dissociation limit. Today, it is this “missing link” that prevents *any accurate experimental* test of Eq. (1).

But, on the basis of experiments, there is a consensus that Eq. (1) is generally valid to within, say, a factor of 3. In addition, one has learned when one should expect exceptions from this rule: van der Waals molecules exist, for which the energy transfer between the hard and soft modes is the rate

determining step, not the crossing of the outer transition state.^{22,23} Individual decay rates of state selected single resonances also do not behave as Eq. (1) prescribes: they may differ by orders of magnitude (cf. Ref. 24). So this is all very gratifying, but cannot be the final answer to the title question.

If one asks whether one can test RRKM theory at a much higher level of accuracy, one must, therefore, compare theory with more exact theory, and this can be done for realistic molecular models only classically. This is what we propose to do in the case study of this paper. We compute $k(E, J)$ from phase space volumes and densities obtained by Monte Carlo integration, and compare them with data derived from classical trajectories. The reader is warned already here that under $k(E, J)$ derived from trajectories, we do not understand the differential " $t=0$ rate," which is hard to get numerically and should trivially coincide with the RRKM rate. Since the intention of RRKM theory is to predict the decay rate of long-lived complexes, and not of short direct collisions, the $t=0$ rate is not relevant for it whenever this rate differs from the *sustained rate*, which one derives from the decay of the bulk of started trajectories. We will see below, that, indeed, these rates are different even though the sustained decay is exponential.

Both calculations use exactly the same potential, for which we take the diatomics-in-molecule (DIM) approximation of the H_3^+ potential. Actually, we treat the system HD_2^+ because its two different decay channels allow additional tests. The selected energies are 0.5, 1.0, and 1.5 eV (measured from the first dissociation threshold), which amounts to 1/10 to 3/10 of the well depth for $J=0$ (4.76 eV). The total angular momentum is taken from 0 in steps of $5\hbar$ to the limit $J_{\max}(E)$, above which dissociation at the given energy is no longer possible.

We find that $k(E, J)$ computed from Eq. (1) is not completely correct, but deviates up to 50% from the true trajectory value. The deviation depends heavily on J , and changes sign near $J=20$. This alone precludes any simple explanation. After thoroughly checking all assumptions underlying Eq. (1), we found that the deviations can be explained quantitatively by what dynamically can be characterized as "direct trajectories," which do not belong to the ergodic ensemble that is presupposed in RRKM theory. Necessary corrections of similar type have also been discussed in Ref. 25. This behavior is the time-reversed counterpart to the phenomenon of "induction time," i.e., the fact that the establishment of a statistical complex on collision needs a finite time. We have discussed this in a former paper.²⁶

For completeness, we note that for transition state (though not RRKM) theory quantum versions have indeed been tested against more exact quantum theory, i.e., scattering theory.^{6,27} However, most of these calculations were of limited scope (e.g., collinear), neither of them computed specific rates, and all use approximations to compute quantum values of the function $N^\ddagger(E, J)$ in view of the problems discussed above. So they are not very stringent tests of the validity of transition state theory (TST) in the sense of this paper.

The paper is organized as follows: In Sec. II, we de-

scribe our methods to compute k_{RRKM} from phase space integrals and k_{tr} from the trajectories. Section III presents our results, in particular, it describes the different (sometimes very small) corrections, which must be applied to the raw results, because other assumptions underlying Eq. (1) are not completely fulfilled. Section IV presents a discussion and conclusions.

II. COMPUTATIONAL METHODS

A. Phase space integration

The evaluation of Eq. (1) has been performed by Monte Carlo integration of the relevant phase space volumes, i.e.,

$$k_{\text{RRKM}} = \frac{\Gamma^\ddagger(E, J)}{\partial \Gamma(E, J) / \partial E}, \quad (2)$$

where $\Gamma^\ddagger$ is the phase space volume at the transition state and Γ is that of the molecule bounded by the reaction coordinate $R^\ddagger$ of the transition state. Reaction coordinates are defined here as the asymptotic Jacobi coordinates, i.e., the distances from the atomic product to the center of mass of the diatomic one. Actually, HD_2^+ has three transition states, two of which are equivalent, and the whole calculation has to be done in three parts, which can be distinguished by the value of the smallest interatomic distance. The position $R^\ddagger$ of the transition state has been determined in each case variationally by minimizing the phase space volume $\Gamma^\ddagger(E, J, R)$ "orthogonal" to the reaction coordinate with respect to this coordinate, starting from the barrier maximum of the minimum effective potential $U_j^{\text{min}}(R)$ (for a definition, see Ref. 28 or Ref. 29). The position of $R^\ddagger$ is a critical one because the denominators in Eqs. (1) and (2) depend almost linearly on it. Therefore, it is also clear that this position does not at all minimize the rate k itself.³⁰ The derivative in the denominator in Eq. (2) is performed by fitting $\Gamma(E)$ to a power law in $E - E_b$, where E_b is the barrier energy [which is a very good representation of $\Gamma(E)$ for limited ranges of E], and taking the analytical derivative of the fit.

Other details of our integration procedure have been described in former papers.^{17,31,32} An essential means to reduce our computing time by one order of magnitude was the use of quasirandom instead of pseudorandom numbers.³² The accuracy of the integrations was controlled (generally to stay below 1% for the raw integration) by prescribing the number of hits (not trials) in the Monte Carlo procedure. It was checked by computing the variance of ten partial calculations.

B. Trajectory calculations

The true (or trajectory) rate of unimolecular composition k_{tr} was computed as the inverse of the average lifetime $\tau(E, J)$ of classical trajectories, which were started from a microcanonical ensemble. The realization of such an ensemble is a nontrivial task. Therefore, starting with the pioneering work of Bunker and Hase,³³⁻³⁶ many methods have been devised to produce good microcanonical ensembles.^{8,36-39} Only recently a method to prepare a microcanonical ensemble with fixed J was published,³⁸ which is not approximative and yields unweighted points. At that

time, we had already started our work, and for simplicity (and because we wanted unweighted points) employed the brute force method of drawing random points in phase space and rejecting all those which did not lie within an energy shell of small, but finite width (in general 0.01 eV, but we used also 0.002 eV for tests to assess the possible error). Because lifetimes depend exponentially on E , but seemingly not so much on the equidistribution of initial conditions,⁴⁰ we then normalized the last drawn momentum p_R to produce the exact total energy. From one such set of initial coordinates, *four* trajectories could be started, differing in the signs of the momentum vector $\mathbf{p}$ and its component p_R (computed at last). Note that the computing time for the collection of sets of initial conditions in this way is comparable to that for the trajectories themselves.

For every combination of E and J , we computed between 5000 and 20 000 trajectories with our standard program (Refs. 41, 42, and earlier papers cited therein). The lifetime t of a single trajectory was defined as the time from its start to the first crossing of one of the three transition states, defined as described above. (Recrossing is discussed below.) Trajectories which did not decay within 1 ps were stopped uncompleted. If the assumptions underlying RRKM theory are valid, one expects the probability density of trajectory lifetimes to obey an exponential law, viz.

$$P(t)dt = \frac{1}{\tau} e^{-t/\tau} dt. \quad (3)$$

In this case, the rate $k(E, J)$ can be computed either as the “ $t=0$ intercept”³⁵

$$k(E, J) = \lim_{t \rightarrow 0} P(t), \quad (4a)$$

or as the reciprocal of the average lifetime

$$\bar{\tau} = \int t P(t) dt. \quad (4b)$$

While Eq. (4a) should be trivially fulfilled for the decay of a microcanonical ensemble, taking the limit numerically is error prone, not to say impossible without any assumption about the functional behavior of $P(t)$. Moreover, we have stated already in the Introduction that it is the sustained rate, determined from the bulk of the decaying ensemble, which we are after, not the rate at $t=0$.

The trajectory data can be fitted very well to a single exponential. However, if one looks very carefully, one sees that the $t=0$ rate (taken from an interval of, say, $t=0$ –100 fs) is, indeed, somewhat *faster or slower* than the bulk rate (taken from the interval 100–1000 fs), and that it agrees with the RRKM rate within its large error limits. In Sec. III B 3, we will discuss ensembles of trajectories from which “direct trajectories” have been removed. In this case, the exponential fit has been limited to the interval from 150 to 1000 fs, since the early decays are now missing. In this interval, $P(t)$ could no longer be distinguished from a single exponential. Note that the differing $t=0$ rate influences the average rate very little. The average decay times derived from the full

range are barely (less than 2%) different from those derived from the restricted range. We have, therefore, in all cases used Eq. (3) for fitting τ to the data.

Two methods have been used to extract the average lifetime from a set of trajectories. In most cases, we used the traditional method of distributing the values of t into a histogram $N_i = N(t > t_i)$ of the integral distribution, and to fit a straight line to the logarithm of the data. It is well known that the error derived naively from this regression underestimates the error of τ strongly. The reason lies in the correlations that are introduced into the integral distribution when it is produced from the differential one. Analysis of variance between the lifetimes obtained from independent subgroups of trajectories (e.g., 14×800 trajectories) showed that the nominal errors of the slope of the regression line must be multiplied by a factor of about 6 to become a realistic estimate of the error. This has been done in all reported results.

From its definition, the easiest method to determine τ would certainly be just to take the average lifetime of the trajectories in a set. However, to do this, *all* trajectories must have been completed. This condition is seldom met. We need, therefore, a method to estimate τ from an ensemble in which only lifetimes up to a certain maximum $t_{\max}$ have been sampled. The histogram method is such a method as long as the fraction of unknown lifetimes is small enough. This is not so for energies near threshold, when τ becomes very large, but the increasing integration error and the heavy demand on computer time prevents the calculation of longer and longer trajectories.

A much more direct method utilizing every single known lifetime t_i can be derived from the general maximum likelihood method.⁴³ Since we never saw this result published, we supply here a short derivation. We divide the time interval from 0 to $t_{\max}$, within which all decay times t_i are known, into M small time intervals Δt . Assuming that N_0 trajectories have been started at time zero and that the decay is exponential, i.e., it has the probability density given by Eq. (3), the logarithm of the likelihood that Z intervals at times t_i contain a decay and N intervals at times t_k do not contain one is

$$\ln L = \sum_1^Z \left(\ln \frac{N_0 \Delta t}{\tau} - \frac{t_i}{\tau} \right) + \sum_1^N \ln \left(1 - \frac{N_0 \Delta t}{\tau} e^{-t_k/\tau} \right). \quad (5)$$

Here, we have assumed that $M = N + Z$ is so large that the probability that any interval contains two or more decays is negligible. (Indeed, we will soon let $M \rightarrow \infty$.) Setting the derivative of Eq. (5) with respect to τ to zero, and after some manipulations, we take the limit $M \rightarrow \infty$ in the expression $(N_0 t_{\max})/(M\tau)$ (but not in N/M), and get the implicit equation

$$\tau = \bar{t} + \frac{N_0 \tau}{Z} \sum_1^N \frac{\Delta t}{\tau} \left(1 - \frac{t_k}{\tau} \right) e^{-t_k/\tau}. \quad (6)$$

Here, $\bar{t} = (1/Z) \sum t_i$ is the average lifetime of the finished trajectories. The above limit implies $\Delta t \rightarrow 0$, so we change from sum to integral, which can be evaluated with the final (implicit) result

FIG. 1. Mean lifetime (inverse unimolecular decay rate) $\tau(E, J) = 1/k(E, J)$ of HD_2^+ vs total angular momentum for three different total energies (a) 0.5; (b) 0.5 (linear scale); (c) 1.0; and (d) 1.5 eV. (Full line) Trajectory result; (short dashed) uncorrected RRKM theory; (long dashed) RRKM, corrected for direct trajectories. Errors of the uncorrected data are smaller than the markers.

$$\tau = \bar{t} + t_{\max} \cdot \frac{N_0}{Z} e^{-t_{\max}/\tau}. \quad (7)$$

It is easy to verify that this formula has the correct limits for very short and very long observation times. It can be solved for τ by iteration starting with the first order result for $\tau \gg t_{\max}$, viz., $\tau = t_{\max} N_0 / Z$, which we had used earlier.⁴²

The error of this maximum likelihood estimate can be similarly obtained in the usual approximation.⁴³ It turns out that in both limits ($\tau \gg t_{\max}$ and $\tau \ll t_{\max}$), the relative error of τ is $1/\sqrt{Z}$, where Z is the number of *observed* decays, and elsewhere differs only to second order. For the bulk of our data, the use of Eq. (7) was not needed, and we did not repeat the evaluations done with the histogram method but it was essential for the computations at low energies discussed at the end of Sec. III B.

III. RESULTS

A. The uncorrected RRKM data

The uncorrected data from the computations described so far are shown as plots of $\tau(J)$ in Figs. 1(a)–(d), curves τ_{RRKM} and τ_{tr} . The statistical errors are in all cases less than 2.5%, which is less than the size of the dots. The general behavior of such curves was known.⁴² While we have no dynamical explanation for the innocuous, almost linear in-

crease of τ at low J , we know in statistical terms that it comes from a subtle compensation between $N^\ddagger(J)$ and $\rho(J)$, which both increase with J , but at different rates. The behavior for large J , on the other hand, is easily understood. At some maximum angular momentum $J_{\max}$, the centrifugal barrier reaches the total energy E and closes the channel, letting $\tau \rightarrow \infty$ and $k \rightarrow 0$. In our case, this happens at $J/\hbar = 61.0, 77.4$, and 88.7 , valid for $E = 0.5, 1.0$, and 1.5 eV, respectively.

It is sometimes argued that one should be able to compute the J dependence of $k(E, J)$ by treating the rotation adiabatically, i.e., taking into account only the decrease of the available energy by the rise of the centrifugal barrier (cf. Ref. 44, or, e.g., Chap. 3.8 of Ref. 5), in mathematical terms

$$k(E, J) = k[E - E^\ddagger(J), \quad J = 0]. \quad (8)$$

Figure 2, which presents the rate $k(E, J)$ vs J at fixed *energies above the respective barriers*, shows that this is not at all the case, and deviations of more than a factor of 2 can be seen. In this system (and probably many real ones) the so-called K rotor couples strongly with vibration, and that already at very low J . This is also easily observed in the trajectories. It has the additional consequence of promoting chaotic dynamics strongly (cf. Ref. 45).

FIG. 2. Uncorrected RRKM rates as a function of total angular momentum for fixed values of the energy $E - E_b(J)$ above the barrier.

In Ref. 42, $\tau(E, J)$ was computed from *scattering trajectories* instead of a microcanonical ensemble. A comparison shows that both sets of data agree with each other to within the larger error bounds of the older computation.

While it was considered gratifying to see that the general behavior of τ_{RRKM} agrees with that of τ_{tr} without any fitting, we still must note that both curves differ by more than the tenfold combined error and that they do it in a very systematic way. We must now try to find out the cause of this deviation. Any simple explanation is ruled out already by the fact that the deviation changes sign as a function of J .

B. Corrections for nonstatistical behavior

In view of the discrepancies just mentioned, we must at first check whether the premises of RRKM theory are fulfilled for our system. They can be stated as follows:

(a) A transition state exists with reaction coordinate $R^\ddagger$ separating the activated molecule from the products. The R -dependent part of the kinetic energy is separable from the other modes at $R^\ddagger$, and $R^\ddagger$ is a "point of no return."

(b) The full phase space of the excited molecule must be equally available for decay, i.e., there are no "bound states in the continuum."

(c) All modes in the activated complex must be "strongly coupled." That means their dynamics must not only be ergodic, but the energy redistribution, i.e., the intramolecular vibrational redistribution (IVR), and the redistribution of the available rotational energy, must be *fast*. In other words, there must be no bottlenecks in the phase space with transmission rates slower or comparable to the decay rate.

We will discuss these points in order. This discussion must, naturally, be in dynamical terms. Tests whether these assumptions are met must, therefore, be decided by the observation of trajectories.

1. The transition state as a point of no return

Since our transition state is "loose," the separability of the motion along R will not be a bad assumption. Its consequence that $R^\ddagger$ is a point of no return is easily checked. All

our trajectories have been run until the products were separated by 7 Å, and the number of trajectories which recross $R^\ddagger$ has been counted. Their fraction is strongly dependent on J . We find zero recrossing for $J < 10$, and a triangular distribution for larger J , peaking at 0.3% for $E = 0.5$ eV, $J = 30$; 1.1% for $E = 1$ eV, $J = 39$; and 3.7% for $E = 1.5$ eV, $J = 47$. The average fractions are about 1/4 as big as the peaks, i.e., always smaller than 1%. Recrossing *prolongates* the trajectory lifetimes, in the most extreme case ($E = 1.5$ eV, $J = 45$) by 5%. Apart from a wrong sign and an insufficient size, recrossing can anyway not explain the deviation of the RRKM result because we have always taken the *first passage time* to define τ_{tr} , and this is what RRKM theory tries to calculate. We conclude that recrossing is of minor importance in our system and cannot contribute anything to explain the discrepancies between τ_{RRKM} and τ_{tr} .

2. Bound regions in phase space

It is well known that in molecules such as H_3^+ , the phase space may contain stable periodic orbits surrounded by finite bound regions of phase space not connected with the ergodic part of it. Trajectories started in those regions never lead to dissociation, even for sufficiently high E . For H_3^+ , one such region is well known; it surrounds the large amplitude bending motion dubbed the "horseshoe orbit,"³¹ which exists for all isotopomers. (Actually, a whole group of such orbits exists,⁴⁶ scars of which have also been seen in quantum calculations.⁴⁷) Such regions are not available for decay; one must, therefore, subtract their volume from $\Gamma(E, J)$ before computing $\rho(E, J)$ and $k(E, J)$.⁴⁸

The estimation of their phase space volume is not easy except for systems of two degrees of freedom. If one could follow all trajectories for times t_{max} much longer than the average lifetime τ , one could argue that the fraction P_b which does not decay within t_{max} must consist of such bound orbits. However, it is generally difficult to meet this condition. The following argument allows, however, to estimate the fraction P_b : We look for *pairs* of trajectories started from the same position in "forward" and "backward" directions, i.e., with momenta $\mathbf{p}$ and $-\mathbf{p}$, and determine as a function of t_{max} the fractions P_1 that *one* branch of a pair does not decay within t_{max} and P_2 that *both* branches do not decay. We assume that both branches of the trajectory are statistically independent, if it belongs to ergodic phase space. This should be the case whenever the unimolecular decay is statistical at all. We define the probability $P_{\text{nd}}(t_{\text{max}})$ that we do not observe the decay before t_{max} . Then we get

$$P_1 = P_b + (1 - P_b)P_{\text{nd}}$$

and

$$P_2 = P_b + (1 - P_b)P_{\text{nd}}^2, \quad (9)$$

from which we can calculate

$$P_b = \frac{P_2 - P_1^2}{1 - P_2 - 2P_1}. \quad (10)$$

Since P_1 and P_2 obey a binomial distribution, one can also calculate an error for P_b . An example for the behavior of

FIG. 3. Probability P_b of bound trajectories computed according to Eq. (10) for $E=0.5$ eV, $J=0$ vs the cut-off time for long trajectories.

$P_b(t_{\max})$ is shown in Fig. 3. We find that P_b almost never differs significantly from zero, but we include it in our corrections whenever it surpasses 1%.

3. Incomplete ergodicity and direct trajectories

It is well known that complete ergodicity of the non-bound phase space cannot be guaranteed for every triatomic molecule. For example, it is known that for a two degrees of freedom, collinear ABC molecule, ergodicity depends in a nonmonotonic way on the mass ratios even if the potential well is simple.^{41,49} For certain mass ratios, the system decays exponentially with approximately the RRKM rate; for others it decays nonexponentially with a fast onset and a very slow tail. Another example are certain van der Waals complexes (generally with very dissimilar normal mode frequencies and/or masses), which decay exponentially, but not with the RRKM rate, because their limiting bottleneck is internal rather than equal to the the outer transition state.^{22,23} Ergodicity seems also to be prevented by a “heavy mass barrier” in chainlike molecules^{50,51} (for a recent experiment, see Ref. 52).

For the full triatomic molecule with six degrees of freedom, complete ergodicity cannot easily be assured, except by performing such global tests, as we are doing here. Exponential decay alone is a necessary, but not sufficient condition for ergodic behavior. On the other hand, H_3^+ and its isotopomers are not expected to have slow or incomplete IVR. They have a simple smooth potential well, similar normal mode frequencies (in our case HD_2^+ in $J=0$ has normal modes of 2934, 2100, and 2268 cm^{-1}), and in many trajectory studies, never any indication was seen that an internal barrier in phase space might exist.

In what follows, we show that the differences between the RRKM rate and the true rate *can* be explained by a specific deviation from ergodicity, which may be described as the existence of “direct trajectories.” We call a trajectory direct, which after its start from the microcanonical ensemble crosses the transition state right away, and whose motion, therefore, does not interact strongly with the other modes of the system. Of course, we must *define* “direct” quantitatively. As a pragmatic measure for this property, we take a

FIG. 4. Percentage of direct trajectories for $E=0.5$ eV as a function of J . (Solid) P_{dir} (activated molecule); (dashed) $P_{\text{dir}}^{\ddagger}$ (transition state).

maximum number of “minimum exchanges,” i.e., changes of the identity of the smallest of the three interatomic distances.⁵³ This is a dimensionless measure, which has the advantage that it is not mass dependent (as an explicit time limit would be), and we have discussed before⁵⁴ that it is also equivalent to a criterion based on the divergence of neighbouring trajectories.⁵⁵ In this as in former papers, a trajectory is called “direct” if it performs less than eight minimum exchanges before it decays.

Note that we must determine two fractions— P_{dir} for the activated molecule in order to correct $\rho(E, J)$, and $P_{\text{dir}}^{\ddagger}$ for the transition state to correct $N^{\ddagger}(E, J)$. The first fraction P_{dir} is nothing other than the microcanonical average of the characteristic function $f_{\text{dir}}(\Gamma)$, which is 1 if the trajectory has less than eight minimum exchanges between start and decay, and 0 otherwise. For $P_{\text{dir}}^{\ddagger}$, the translation into trajectory language is somewhat more difficult. However, one can see from the flux formula for $k(E, J)$ (cf., e.g., Ref. 56) that $N^{\ddagger}$ stands for a *flux*, which can be represented by trajectories started inwards at the transition state, which have been weighted with the velocity $\dot{R}$. That is, we take

$$P_{\text{dir}}^{\ddagger} = \frac{\int d\Gamma^{\ddagger} f_{\text{dir}}(\Gamma^{\ddagger}) \cdot |\dot{R}| \cdot \delta[E - H_J(\Gamma^{\ddagger})]}{\int d\Gamma^{\ddagger} |\dot{R}| \cdot \delta[E - H_J(\Gamma^{\ddagger})]} \quad (11)$$

Figure 4 shows both fractions for $E=0.5$ eV. They reach a maximum of 25% for $E=0.5$ eV, and 65% for $E=1.5$ eV, but compensate partially in Eq. (1). It is their *different* behaviour as a function of J which leaves a net correction to $k(E, J)$ that even changes sign near $J=20$. We finally get

$$\tau_{\text{RRKM cor}} = \tau_{\text{RRKM}} \cdot \frac{1 - P_b - P_{\text{dir}}}{1 - P_{\text{dir}}^{\ddagger}} \quad (12)$$

where we use P_b only in those few cases where it is significantly different from zero.

Before we discuss this further, we demonstrate that the correction is robust against variations in the definition of a

FIG. 5. Correction factors (○) $1-P_{\text{dir}}$ and (◇) $1-P_{\text{dir}}^{\ddagger}$, and (◻) their ratio $f=(1-P_{\text{dir}})/(1-P_{\text{dir}}^{\ddagger})$ vs the number of minimum exchanges used to define a direct trajectory.

direct trajectory. Figure 5 shows the correction factor of Eq. (12) for $E=1.0$ eV, $J=45$ (one of the largest which we find) as a function of the number of minimum exchanges used to define direct trajectories. One sees that above five minimum exchanges, the correction is practically constant. This justifies the arbitrariness involved in taking just eight minimum exchanges as the limit.

For energies below 0.5 eV, it becomes more and more difficult to determine the trajectory lifetime because less and less trajectories can be calculated until their decay. Utilizing the second method of evaluation mentioned in Sec. I B, we have, nevertheless, computed one example, in which we decrease $E-E_b$ down to 0.1 eV. This calculation was for $J=10$, where E_b is 2.247 meV. One sees in Fig. 6 that for $E-E_b \rightarrow 0$, both fractions of direct trajectories tend to zero, and that their ratio and that of the uncorrected lifetimes tend to one. This is expected because “at threshold, transition state theory is exact.”⁵⁷

The final, corrected τ_{RRKM} is included in Figs. 1(a)–1(d), and discussed further in Sec. IV.

4. Isotopic branching ratio and product distributions

Though product distributions are not in the focus of this paper, we want to show two results which came out as a byproduct of our computation. The system HD_2^+ has two decay channels $\text{D}^+ + \text{HD}$ and $\text{H}^+ + \text{D}_2$. Let us call their fractions P_1 and P_2 , so that $2P_1 + P_2 = 1$ and

$$P_2(E, J) = \frac{N_2^{\ddagger}(E, J)}{N^{\ddagger}(E, J)}. \quad (13)$$

P_2 is shown in Fig. 7. For comparison, we also show a simple approximation, in which the system is modeled as a separable combination of a diatomic oscillator with a 2D rotator. In this case, one gets

$$P_2(E, J) = \frac{[E - E_2^b(J)]^2}{[E - E_2^b(J)]^2 + 2\alpha^{3/2}[E - E_1^b(J)]^2}, \quad (14)$$

where $\alpha=2/3$ is the ratio of the reduced masses of HD and D_2 . The agreement of this curve with the uncorrected RRKM

(a)

(b)

FIG. 6. (a) Data points and regression lines for $1-P_d$ and $1-P_d^{\ddagger}$ and their ratio f vs the energy above the barrier. P_d and $P_d^{\ddagger}$ are the fractions of direct trajectories for the activated molecule and the transition state, respectively. (b) (●) Ratio $\tau_{\text{RRKM}}/\tau_{\text{tr}}$ of (uncorrected) RRKM lifetime to trajectory lifetime, (◇) correction factor $(1-P_{\text{dir}})/(1-P_{\text{dir}}^{\ddagger})$, and (■) their product (expected to be 1) vs the energy above the barrier. Both plots are for $J=10$.

result shows again how loose the transition state is. However, the *true* fraction P_2 is different by a J -dependent factor, which can be as big as 2. Only if we correct the channel

FIG. 7. The fraction P_2 of molecules dissociating into the channel $\text{H}^+ + \text{D}_2$ at 1.0 eV activation energy vs total angular momentum. (Solid) Trajectory data; (short dashed) uncorrected RRKM; (long dashed) corrected RRKM; (dotted) approximation (14).

FIG. 8. Average energy disposal of decaying HD_2^+ complexes at $E = 1.0$ eV as a function of J . (Full line) E_{vib} ; (dashed) E_{rot} ; (dotted) $[E - E_b(J)]/3$. Not shown is $E_{\text{trans}} = 1.0 - E_{\text{vib}} - E_{\text{rot}}$. The error bars indicate the rms widths of the distributions.

values $N^\ddagger$ in the numerator and the denominator of Eq. (13) by the respective factors $(1 - P_{\text{dir}}^\ddagger)$ do we get agreement with the trajectory data.

Finally, from the trajectory calculations, we have also determined the fractions of total energy deposited in translation, vibration, and rotation. Figure 8 shows the result at fixed $E_{\text{tot}} = 0.5$ eV. It demonstrates that these fractions are not at all each 1/3. This can be understood as follows: For large J , the available energy at the transition state ($\approx$ the barrier) is only $E_{\text{tot}} - E_b(J)$, a function that decreases with J . One-third of this value is also plotted in Fig. 8 and one observes that vibration and rotation get just this fraction and not any more during the further decay. All energy gained after the barrier goes additionally into translation. For medium J , the 1/3 rule is approximately correct, while for $J < 10$, rotation becomes partially adiabatic, and we find $E_{\text{tr}} \approx E_{\text{vib}} \approx 2E_{\text{rot}}$.

In experiments, one will generally have an ensemble of total angular momenta, which depends on the preparation of the activated complex, and which is not necessarily microcanonical. The distributions $P(J)$ for HD_2^+ activated in collisions have been discussed in Ref. 26 and references cited therein. In a typical case, not forgetting the weight $2J+1$, an average over J will lead to a translational energy which is larger than $E_{\text{tot}}/3$ by an appreciable factor.

IV. DISCUSSION

RRKM theory is one of the most valuable statistical theories in chemical physics, so it is certainly worthwhile to test it as accurately as one can. We have discussed in the Introduction that such a test at an accuracy level of a few percent can these days be done only by comparing classical RRKM theory with classical dynamical (trajectory) calculations. This scheme has been used before since the pioneering papers by Bunker and co-workers,^{33–35} but never for specific rates $k(E, J)$, and never at the accuracy which we could obtain (thanks to progress in computer manufacturing, to be sure).

It is still nearly impossible to perform such tests exhaustively, i.e., for any size of molecule, any type of potential, and any mass ratio. We could present here only a case study. It simulates the decay of H_3^+ well enough to be comparable to experiments, if they were available. It should also be sufficiently representative for the unimolecular decay of other typical triatomic molecules such as CH_2 , NO_2 , and SO_2 , and probably also for H_2O with its more extreme mass ratio, and CO_2 , which has a linear equilibrium conformation. A hint that this is so can be seen in the smooth behavior of the unimolecular lifetime if one distorts the equilibrium shape of a triatomic molecule.⁵⁸ Other types of molecules do not belong to this category. Some have been mentioned in the Introduction, and we want to add here the collinear model of CCH so thoroughly investigated by Hase and co-workers.^{59–61} How much these results can be extended to larger molecules, we can only speculate. Checks along the lines of this paper are, at least, feasible for four- and, perhaps, five-atomic ones.

Our first remark is that, until now, an agreement of 20% or 60% between trajectory and RRKM results was “seen as good agreement” (cf. Ref. 5, p. 121). In this study, we have shown that this level of agreement extends also to the specific rates $k(E, J)$. However, we have also shown that at a much higher level of accuracy, there are systematic, reproducible deviations of the RRKM rates from the true ones. It is remarkable that these differences exist even at activation energies of only 10% of the well depth.

A systematic search for possible causes of this effect led us to the influence of a special form of incomplete ergodicity, describable in dynamical terms as the influence of direct trajectories in the microcanonical, J -selected ensemble. We have also shown that we can apply a correction for this effect to the RRKM results if we know the dynamics, and that this leads to perfect agreement of statistics and dynamics at the level of about 3%. Note that it is the error in the corrections which increases the error estimate for the corrected values so much over that of the raw data.

How can one understand this effect? Let us apply time reversal to unimolecular decay. We consider collisions which form a “long-lived complex,” defined by postulating the statistical independence of the decay dynamics from the dynamics of formation (except, of course, for the conserved quantities E and J). For sufficiently strong coupling between all degrees of freedom in the complex, we may assume that it behaves as a microcanonical ensemble, and its unimolecular decay can be described by RRKM theory. But it was formed from educts which are *not* a microcanonical ensemble. Therefore, to form the “statistical complex,” some energy (and also some partial angular momentum) must be exchanged among the six degrees of freedom, i.e., physically between the atoms. *This interaction needs some time*, which is often called the induction time. It is measured (starting with the crossing of the transition state by the incoming atom) as the average time needed until the properties of the collision complex become equilibrated. We have analyzed this for H_3^+ in a recent paper²⁶ with the result that the order of magnitude for this delay time in our system is 50 fs. Now we turn back to unimolecular decay. From time reversal, we

must conclude that also in the decay, some time is needed to transform the microcanonical activated complex to the non-microcanonical products. Exclusion of direct trajectories then means that we exclude just that part of the microcanonical ensemble which will be no longer microcanonical after some 50 fs. This is in agreement with our exclusion of trajectories, which have less than eight minimum exchanges, since the time per minimum exchange is about 8 fs in H_3^+ .

What we have just described has been discussed in a more formal way by Dumont and Brumer.²⁵ These authors showed that for a relaxation time different from zero, there will always be a "nonstatistical" component in the unimolecular lifetime distribution, which makes the effective rate faster than that from Eq. (1). This is in contrast to standard wisdom, which says that the rate should always be slower than the RRKM rate because of recrossings. Note, however, that this wisdom does not consider a finite relaxation time, which is the central argument of Dumont and Brumer. These authors also discuss a specific model for the lifetime of a complex between its formation and decay, which they call the "delayed lifetime gap model." Their decay law could, however, *not* be fitted to our data, which, to remember, are for the decay of a microcanonical ensemble.

Finally we should mention that we are, of course, aware of the logic of our treatment. The corrections of Eq. (1), which we applied, utilize the dynamics of the system which statistics wants to avoid. So, they are not constructive as long as they cannot be translated into purely statistical terms. We think that in view of Ref. 25, this may not be fully impossible.

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