# **Dissociation of Small Molecules:** Direct Dissociation or Statistical Energy **Redistribution?**

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Dissociative processes in highly excited small molecules and radicals are studied by translational spectroscopy. Fragmentation reactions are identified, and insight into their mechanisms is gained by the differential measurement of the fragment kinetic energy. The reactions under study are induced by dissociative charge exchange. The dissociation of CH<sub>3</sub>Cl with an internal energy between 6.1 and 6.9 eV into  $CH_3^{\circ} + Cl^{\circ}$  proceeds via a repulsive surface, converting most available energy into kinetic energy. The dissociation of  $CH_3CO^*$  with an internal energy above 1.9 eV into  $CH_3^* + CO$  is preceded by energy scrambling. The kinetic energy release is governed by the dynamics of the reaction: a simple kinematic model for the conversion of bending motion into fragment translation is consistent with the measured spectra.

## Introduction

Mechanisms of energy flow in excited molecules are of great importance for the occurrence, rate, and specificity of a chemical reaction. The fundamental study of these mechanisms on the molecular level is becoming increasingly feasible due to advances in the experimental techniques. The most direct way to study the fate of internal energy is to monitor the different forms of energy into which it can be converted. If the excitation energy leads to dissociation, the fragments can be detected and their internal and translational energy can be measured. A fundamental difference between intramolecular relaxation processes and dissociation processes is that the latter open up the possibility for conversion of internal reactant energy to product translational energy.

Theory is keeping pace with the advent of more and more detailed experimental data. The interaction of two bound atoms can be described with a high degree of accuracy, and many principles governing a reaction have been identified. Due to their complexity, the intramolecular dynamics of large polyatomic systems can in general only be described by statistical theories. The most widely used of these is the quasi-equilibrium theory. A molecule is described as an isolated system with constant energy. The population of each allowed quantum state in the molecular phase space is assumed equally probable (the "quasi-equilibrium" condition). Such a system is named a microcanonical ensemble in statistical mechanics, and the equations developed in that field are employed in the quasi-equilibrium theory. Therefore this theory depends on the main assumption of statistical mechanics, that the number of states be large.

Systems of an intermediate size, where the transition between these two extremes takes place, are therefore of great interest. Fundamental reaction processes can be observed and interpreted without too much ambiguity due to the multiplicity of intramolecular degrees of freedom. This paper describes work on two such molecules: CH<sub>3</sub>Cl and CH<sub>3</sub>CO<sup>•</sup>. We measured distributions  $P(\epsilon_d)$  of the kinetic energy release  $\epsilon_d$  from fragmentation reactions of the type (1). Energy measurements are a more stringent test of a theory than the common rate constant measurements. The fragmenting molecules were highly excited neutral molecules AB\*, produced by charge exchange of the corresponding ions  $AB^+$  with alkali metals M. The fragmentation reaction is symbolized by

$$\underline{AB^{+}} + M \rightarrow \underline{AB^{*}} + M^{+} \rightarrow \underline{A} + \underline{B} + M^{+} + \epsilon_{d} \qquad (1)$$

where underlining stands for a fast particle.

Methyl chloride  $(CH_3Cl)$  is a pseudotriatomic molecule linear in its ground and some excited states. Photodissociation of CH<sub>3</sub>Cl as well as of CH<sub>3</sub>I with 6.4-eV photons yields methyl radicals.<sup>1</sup> For CH<sub>3</sub>I molecules, this process as well as the photodissociation with 5.0-eV photons has been shown to be nonstatistical.<sup>2,3</sup> The

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dissociation of the ion  $CH_3Cl^{++}$  into  $CH_3^+ + Cl^+$  is highly nonstatistical, as evidenced by the single kinetic energy release value measured in PIPECO experiments.<sup>4</sup> This is corroborated by the collision-induced-dissociation experiments of Hop et al., where the m/z = 15 peak was found to be characteristically broadened.<sup>5</sup>

In the acetyl radical ( $CH_3CO^{\bullet}$ ), the equilibrium CCO angle is roughly 120°, while the  $CH_3CO^+$  ion has a linear skeleton.<sup>6,7</sup> Not much is known about the electronic states of the acetyl radical, but an optical absorption stretching from about 200 to 240 nm has been measured by Parkes.<sup>8</sup> Acetyl in an organic glass matrix was reported to absorb at 340, 500, and 540 nm.<sup>9</sup> Recently, its heat of formation was (re)determined by Holmes and Lossing.<sup>10</sup> Isolated acetyl radicals have been formed as neutral fragments of a metastable dissociation<sup>11,12</sup> or from acetyl cations neutralized by collisions with xenon,<sup>13</sup> mercury,<sup>14</sup> and cadmium.<sup>15</sup> The radicals thus formed have been studied by collision-induced dissociative ionization on helium or oxygen target gas. A large fraction of them is found to dissociate within 0.5  $\mu$ s (the flight time between the two reactions) into a methyl radical and a carbon monoxide molecule releasing a large ( $\approx 0.5$  eV) translational energy

The differences in structure and intramolecular behavior between the molecules CH<sub>3</sub>Cl and CH<sub>3</sub>CO<sup>•</sup> are expected to be reflected in their dissociation dynamics and therefore in the kinetic energy release.

#### **Experimental Section**

Descriptions of the translational spectrometer employed for our research and the experimental procedure for measurements have

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Figure 1. Schematic diagram of the measured parameters  $R_A$ ,  $R_B$ , and  $\tau$  and their relation to the experimental parameters L and  $v_0$ . The angle between the fragment velocity vectors is exaggerated for clearness.

been published.<sup>16,17</sup> In short, fast excited neutral molecules AB\* (mass  $m_{AB}$ , beam velocity  $v_0$ ) are prepared by neutralization of a beam of mass-selected ions AB<sup>+</sup>. Charge exchange takes place with an alkali-metal vapor of about 0.1 Pa pressure. The deflection of the center of mass is small (we measured a total beam divergence of  $\leq 10^{-4}$  rad). A possible subsequent reaction is reaction 1. In Figure 1 this is schematically shown for one dissociation event. The kinetic energy  $\epsilon_d$  is divided between the fragments A and B inversely proportional to their masses  $m_A$  and  $m_B$ . This leads to fragment velocities  $v_A$  and  $v_B$ , of which the dependence on the dissociation angle  $\Theta$  is evident from the figure. The two fragments are detected in coincidence by intercepting them after a drift length L with a radial two-particle detector based on multichannel plates. For each detected fragment pair, the radial distances  $R_A$  and  $R_B$  of the fragments and the arrival time difference  $\tau$  between A and B are measured. From these differential quantities, the energy  $\epsilon_d$  and the masses  $m_A$  and  $m_B$  can be calculated. The measured distance between the impinging fragments, which is a distance in the center-of-mass frame, is a measure for the kinetic energy release, while the ratio of the distances  $R_A$  and  $R_{\rm B}$  is a measure of the mass ratio  $m_{\rm B}/m_{\rm A}$ . These relations are expressed by (2), where  $R_{AB} = R_A + R_B$ :

$$\epsilon_{\rm d} = \frac{\mu_{\rm AB} v_0^2}{2} \frac{R_{\rm AB}^2 + (v_0 \tau)^2}{L^2}$$
 (2A)

$$m_{\rm A} = m_{\rm AB} \frac{R_{\rm B}}{R_{\rm AB}} \tag{2B}$$

where  $\mu_{AB} = m_A m_B m_{AB}^{-1}$  is the reduced mass of the fragments. The measurement of many dissociation events yields "neutral mass spectra" and, for each reaction, the corresponding spectrum of the kinetic energy release. From these spectra the dissociation pathways of an excited neutral molecule can be identified and, simultaneously, that part of the excitation energy can be determined which is converted into fragment kinetic energy. The dimensions of the detector ( $R_{min} = 5 \text{ mm}$ ,  $R_{max} = 32 \text{ mm}$ ) place restrictions on the mass ratio of the fragments and the range of kinetic energies. No coincident measurement is possible if one of the fragments is lighter than  $0.14m_{AB}$ . The maximum detectable kinetic energy (for  $\theta = \pi/2$ ) scales with  $m_B/m_A$ . Furthermore, dissociations into more than two fragments can be detected, since they lead to a raised base line in the "neutral mass spectrum" (see Discussion).

The experimental conditions were as follows: ions were created in an electron impact (EI) ion source with variable electron energy, the ion beam energy was set to 4 keV, and target atoms Na, K, and Cs were chosen, with respective IP's of 5.14, 4.33, and 3.89 eV. The drift length L was 1480 or 780 mm, corresponding to measurable  $\epsilon_d$  ranges from 0.11 to 0.80 eV or, respectively, from 0.39 to 2.9 eV. These ranges are calculated for the dissociation of methyl chloride ((5) below), which is the fragmentation reaction with the most unfavorable fragment mass ratio.



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Figure 2. Experimental neutral fragment mass spectrum of  $CH_3Cl^{*+}$  neutralized by Na, showing the fragmentation channel to be  $CH_3^{*+} + Cl^{*-}$ . The mass axis is scaled by the precursor mass. The raised base line at the low mass side of the peak is due to secondary dissociations.

 $CH_3Cl^{++}$  ions were produced by 70-eV EI of the corresponding gas-phase molecules. Acetyl ions were usually 45-eV EI fragments from acetone. Supplementary experiments were run with different compounds which upon electron impact produce acetyl ions. The measurements of methyl chloride and acetyl were performed with Na and K targets and a short drift length. Acetyl was also measured with Na and Cs and a long drift length.

# **Charge Exchange**

Charge exchange (CE) can be employed to produce excited neutral molecules with a well-defined internal energy. The cross sections  $Q_{CE}$  are large, implying that the electron is exchanged at large internuclear distances and thus with little momentum transfer. CE of polyatomic molecules is usually a vertical resonant process. This is evidenced by the dependence of the cross section  $Q_{CE}$  on the collision velocity<sup>18</sup> as well as on the energy mismatch between the IP of the target M and the recombination energy (RE) of the ion AB<sup>+.19</sup> The resonant character of CE leads in the neutralized molecule AB to the preferential population of states with internal energy  $E_0$ , which is defined in (3). It is a common approximation to equate RE of an ion to the IP of the corresponding neutral. For appreciable differences in the structures of the ion and the neutral, this approximation loses its validity. The distribution function P(E) of internal energy E can be approximated by  $Q_{CE}$  for a two-level system:<sup>17,20,21</sup>

$$E_0 = \operatorname{RE}(AB^+) - \operatorname{IP}(M) \approx \operatorname{IP}(AB) - \operatorname{IP}(M)$$
(3)

$$P(E) \propto Q_{\rm CE}(E-E_0) \propto {\rm sech}^2\left(\frac{\pi^2(E-E_0)2^{1/2}}{h\lambda v_0}\right) \qquad (4)$$

where h is Planck's constant and  $\lambda$  is defined by the coupling matrix element  $H_{12}(R) = \exp(-\lambda R)$ . A typical width of P(E) is 0.5 eV. In (4) it is assumed that states with energy E are available. If this condition is not fulfilled, P(E) is obtained by convoluting  $Q_{CE}$  with the density of available states.

#### Results

*Methyl Chloride*. For all targets employed, the detected dissociation pathway of methyl chloride is the loss of the methyl radical:

$$\underline{CH_3Cl^{\bullet+} + M} \rightarrow \underline{CH_3Cl^* + M^+} \rightarrow \underline{CH_3^{\bullet} + \underline{Cl^{\bullet}} + M^+ + \epsilon_d}$$
(5)

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<sup>(19)</sup> Shields, G. C.; Steiner IV, P. A.; Nelson, P. R.; Trauner, M. C.; Moran, T. F. *Org. Mass Spectrom.* **1987**, *22*, 64 calculate the recombination energy of  $CH_3CO^+$  to be 6.32 eV.



Figure 3. Experimental  $\epsilon_d$  spectrum of the reaction CH<sub>3</sub>Cl<sup>++</sup>/Na  $\rightarrow$  CH<sub>3</sub>Cl<sup>+</sup> + Na<sup>+</sup>  $\rightarrow$  CH<sub>3</sub><sup>+</sup> + Cl<sup>+</sup> + Na<sup>+</sup> +  $\epsilon_d$ . The detector cutoff lies at 2.9 eV.



Figure 4. Experimental neutral fragment mass spectrum of  $CH_3CO^+$  neutralized by Na, showing the fragmentation channel to be  $CH_3^* + CO$ . The mass axis is scaled by the precursor mass. The raised base line at the low mass side of the peak is due to secondary dissociations. For a comparison, see Figure 11.

A mass spectrum is shown in Figure 2. A slight background is seen at the low mass side of the discrete peak. The  $\epsilon_d$  spectrum consists of one single peak 0.7  $\pm$  0.1 eV wide at half-height, located at 2.5  $\pm$  0.2 eV for M = Na, and at 3.0  $\pm$  0.3 eV for M = K. As an example, the CH<sub>3</sub>Cl<sup>++</sup>/Na spectrum is shown in Figure 3.

Acetyl. The spectra show for all targets similar results: the neutral mass spectra show the measurable dissociation pathway to be

$$\underbrace{CH_{3}CO^{+} + M \rightarrow CH_{3}CO^{**} + M^{+} \rightarrow}_{CH_{3}^{*} + CO + M^{+} + \epsilon_{d}} (6)$$

with a background at the low mass side of the main peak (Figure 4). Also the  $\epsilon_d$  spectra are very similar in the range from 0.3 to 3.0 eV:  $P(\epsilon_d)$  rises steeply to a maximum at  $\epsilon_d = 0.75 \pm 0.1$ eV and falls off approximately with a power law to the maximum value of  $\epsilon_d$ , which for a Na and K target is situated at 2.5 ± 0.1 and 2.9  $\pm$  0.1 eV. In Figure 5, we give the CH<sub>3</sub>CO<sup>+</sup>/Na spectrum. For Cs, the maximum value was measured with an unfavorable drift length; it was found to be  $2.8 \pm 0.2 \text{ eV}$ . The spectra for the low  $\epsilon_d$  range exhibit more pronounced differences. Spectra are shown in Figure 6A,B for the two targets with the most extreme ionization potentials. The paramount difference is the occurrence of a low-energy tail down to  $\epsilon_d = 0.1 \text{ eV}$  (the apparatus cutoff) with the Na target, which is not seen with the Cs target. Additionally, in the CH<sub>3</sub>CO<sup>+</sup>/Na experiment a weak shoulder superimposed on the main structure in the spectrum was seen at  $\epsilon_d = 1.3 \pm 0.1 \text{ eV}$ , where the concave curvature of the spectrum turns convex.

The energy of the ionizing electrons was changed from 13 to 70 eV, but no differences in the  $\epsilon_d$  spectra were observed. Several



**Figure 5.** Experimental  $\epsilon_d$  spectrum of the reaction CH<sub>3</sub>CO<sup>+</sup>/Na  $\rightarrow$  CH<sub>3</sub>CO<sup>\*\*</sup> + Na<sup>+</sup>  $\rightarrow$  CH<sub>3</sub><sup>\*</sup> + CO + Na<sup>+</sup> +  $\epsilon_d$ . The spectrum is composed from two measurements with long and short flight length *L*, yielding the low-energy (<0.8 eV) and high-energy (>0.8 eV) part of the spectrum.



Figure 6. Experimental  $\epsilon_d$  spectra, exemplifying the different dissociation behavior due to variation in internal energy (A vs B) and fragment mass ratio (B vs C). The low-energy region is selected by measuring with a long flight length L.

experiments were run with different compounds that upon electron impact produce acetyl ions. These compounds were 2-butanone, 2,3-butanedione, and 1,1,1-trifluoroacetone. As electron donors in these experiments we employed Na (drift length 780 mm) and Cs (1480 mm), but the obtained spectra did not differ from the spectra with acetone in the ion source.

To induce a variation in the fragment mass ratio, deuterated acetyl ions (CD<sub>3</sub>CO<sup>+</sup>) were produced from deuterated acetone. Again, the measured dissociation was the one into CD<sub>3</sub><sup>•</sup> and CO. The  $P(\epsilon_d)$  curves were measured with Cs target gas and a drift length of 1480 mm (see Figure 6C). The curve onset and the maximum were shifted to values about 0.1 eV lower than in the spectrum of neutralized CH<sub>3</sub>CO<sup>+</sup> ions, while both curves coincided above  $\epsilon_d = 1.1$  eV.

# Discussion

The compounds under study have been selected in view of their size (intermediate between "small diatomic" and "large polyatomic" molecules), of their structural similarity (a methyl group coupled to a structural unit of about twice the methyl mass) and of the expected difference in molecular complexity (acetyl has 12 internal degrees of freedom, 3 more than methyl chloride). Judging solely from the number of degrees of freedom, a marked but not dramatic difference in their dissociation behaviour is expected. The measured spectra show, however, that completely different dissociation mechanisms are operative. We will therefore discuss the results obtained for the two molecules separately.

Methyl Chloride. The fact that one peak of the kinetic energy release is observed indicates that charge exchange of methyl chloride cations with Na or K atoms populates a narrow energy interval of a repulsive neutral state. The width of the  $\epsilon_d$  peak matches the theoretical width calculated for a two-level system, given by (4). This process of resonant neutralization from a bound ionic state to a repulsive state has been demonstrated previously



**Figure 7.** Schematic potential diagram for the reaction  $CH_3Cl^+/M \rightarrow CH_3Cl^+ + M^+ \rightarrow CH_3^{\bullet} + Cl^{\bullet} + M^+ + \epsilon_d$ . The triangle indicates the optical absorption band at 7.2 eV.<sup>23</sup> The levels K<sub>res</sub> and Na<sub>res</sub> indicate the theoretical resonance energies for M = K, Na according to (3). The dashed lines  $K_{exp}$  and  $Na_{exp}$  indicate the measured peaks. The line FC indicates vertical neutralization. The  $\epsilon_d$  spectrum is the same as in Figure 3.

in collisions of hydrogen molecular ions with a Mg target.<sup>22</sup> The neutral molecule will dissociate by following the slope of the repulsive potential within about half a vibrational period. No time is available for internal relaxation and energy redistribution. This situation can be compared to a so-called "isolated state", which is a concept sometimes called upon in explaining observed deviations from quasi-equilibrium theory. Repulsive states in the suitable energy range are the <sup>1</sup>Q and <sup>3</sup>Q states, which were probed by van Veen et al. in photodissociation measurements on CH<sub>3</sub>I, a molecule comparable to CH<sub>3</sub>Cl.<sup>3</sup> The broad optical absorption band of the transition from the ground state to the Q states stretches from 6.2 to 7.7 eV, with a maximum at 7.2 eV.<sup>23</sup> The  $^1Q$  state correlates adiabatically with the ground-state products methyl and the halogen atom. The  $^3Q$  state correlates with ground-state methyl and the spin-orbit excited atom (see Figure 7). In our spectra, we cannot discriminate between the Q states.

The ionization potential of CH<sub>3</sub>Cl is 11.22 eV;<sup>24</sup> therefore resonant charge exchange with Na or K yields neutrals with an internal energy of 6.08 or 6.89 eV, respectively. The heats of formation of the reactant and products in their ground states are  $\Delta H_{f}(CH_{3}Cl) = -0.85 \text{ eV}, \Delta H_{f}(CH_{3}^{\bullet}) = 1.51 \text{ eV}, \text{ and } \Delta H_{f}(Cl^{\bullet}) = 1.26 \text{ eV}.^{24,25}$  The equation for the kinetic energy release in reaction 1 is

$$\epsilon_{d} = E_{0} - E_{A} + E_{rev} = E^{*} + E_{rev} \approx \Delta H_{f}(AB) + IP(AB) - IP(M) - \Delta H_{f}(A) - \Delta H_{f}(B)$$
(7)

In this equation, exactly resonant charge exchange is assumed. Radiative losses and product energy other than translational are neglected.  $E_A$  is the activation energy of the dissociation, and  $E_{\rm rev}$  is the activation energy for the inverse reaction. Its value is small for most reactions.  $E^*$  is the so-called excess energy of the transition state. The adiabatic dissociation energy  $D_0$  for the A-B bond equals  $E_A - E_{rev}$ . Filling in the above thermodynamical values and assuming ground-state products, (7) leads to expected  $\epsilon_d$  values of 2.46 eV (sodium target) or 3.27 eV (potassium). The  $CH_3Cl^+/Na$  measurement matches the expected value well, but the  $CH_3Cl^+/K$  result lies 0.3 eV below the theoretical value.

For the interpretation of this result, we shall consider the known repulsive states in question. We have drawn, in Figure 7, a schematic potential diagram of the Q states in CH<sub>3</sub>Cl, making use of the available information. For CH<sub>3</sub>Cl, no calculations on the position and shape of these repulsive states have been published. Therefore the potentials are drawn in analogy to the corresponding CH<sub>3</sub>I states,<sup>3</sup> a molecule comparable to CH<sub>3</sub>Cl. The equilibrium C-Cl distances are 1.78 Å in the neutral and 1.71 Å in the ion; they are taken from Herzberg<sup>23</sup> and Shields et al.,<sup>26</sup> respectively.

The small difference between the  $\epsilon_d$  spectra after neutralization by K and Na suggests that the same electronic state is populated in both cases. From the optical absorption, which in CH<sub>3</sub>I is the transition to the <sup>3</sup>Q state,<sup>3</sup> we conclude that the <sup>3</sup>Q state should be positioned at 7.2 eV vertically above the CH<sub>3</sub>Cl ground state. The <sup>1</sup>Q state should, in analogy to the CH<sub>3</sub>I case, lie higher than the <sup>3</sup>Q state at low C-Cl distances. The vertical neutralization for the case that the structures of the ionic and excited neutral methyl chloride are similar is indicated by FC in Figure 7. From the figure, and employing (7), the kinetic energy release is expected to be at least 3.5 eV-a value about 0.5 eV (1 eV) higher than the one measured with the K (Na) target.

We consider this deviation between the expected and the measured kinetic energy. In CH<sub>3</sub>I, the repulsive <sup>3</sup>Q state was photodissociated by van Veen et al.<sup>3</sup> The resulting methyl fragment was vibrationally excited in the  $\nu_2$  "umbrella" mode, with a v distribution peaked at v = 2 and stretching up to  $v \approx 7$ . It can be argued that also in our experiment vibrationally excited methyl is formed. Such vibrational energy would lower the energy available for fragment translation and could therefore account for the difference between the measured energy and that expected for a vertical transition. To account for the energy mismatch, vibrational quantum numbers of v = 8 (for 0.5 eV) and v = 15(for 1 eV) are necessary. Here we use the same  $v_2$  frequency as van Veen et al. (522 cm<sup>-1</sup>). In view of these high quantum numbers, we believe that the energy deviation between theory and experiment is not due to vibrational fragment excitation.

The assumption of similar structures of the methyl chloride ion and neutral is dubious. Shields et al.<sup>26</sup> found in ab initio calculations that the lowest energy structure of the ion is bridged. The vertical transition then cannot simply be drawn in Figure 7. The population of the accessed state can be calculated, if the structures of both the initial and final state are known. Since this is not the case, we carefully conclude from the measured kinetic energy releases that neutralization of CH<sub>3</sub>Cl<sup>+</sup> by Na and K takes place to one or both the repulsive Q states. The level that is populated lies, for the Na target, at least 2.7 eV (3.0 eV for K target) above the ground-state dissociation limit. Vibrational excitation of the fragments is unlikely.

The difference between the  $\epsilon_d$  values measured with Na and K targets is at variance with strictly vertical electron transfer but can be understood from the resonant character of the process. In a strictly vertical transition, the  $\epsilon_d$  value should be the same regardless of the target element. For a strictly resonant transition, the  $\epsilon_d$  difference should be given by  $\epsilon_d(M=K) - \epsilon_d(M=Na) =$ IP(Na) - IP(K) = 0.81 eV, as can be seen from (3) and (7). An intermediate value ( $\approx 0.5 \text{eV}$ ) is found for  $\epsilon_d(M=K) - \epsilon_d(M=Na)$ ; this means that the maximum of the product of the charge-exchange cross section and the Franck-Condon overlap is lying at smaller C-Cl distances for CH<sub>3</sub>Cl<sup>++</sup>/K than for CH<sub>3</sub>Cl<sup>++</sup>/Na. From the different positions of the  $\epsilon_d$  peak and the different C–Cl distances for different targets the steepness of the repulsive potential can in principle be derived. The matching of the  $CH_3Cl^{+}/Na$  result and the theoretical value indicates that the energy difference of initial and final state in the vertical transition equals the IP of Na (5.14 eV).

Acetyl. In this section we will first discuss the electronic states in the acetyl radical which are populated by charge exchange. After that we will derive two distribution functions  $P(\epsilon_d)$  for the kinetic energy release of a statistical dissociation. Firstly,  $P(\epsilon_d)$ is given for the standard model of a stretching motion being converted into translation. Secondly, from a simple kinematic model for the dissociation, the conversion of skeletal bending motion into translation is studied. Implementation of this additional mechanism for kinetic energy into the statistical formulas

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Figure 8. Schematic potential diagram for the reaction  $CH_3CO^+/M \rightarrow$  $CH_3CO^{\bullet\bullet} + M^+ \rightarrow CH_3^{\bullet} + CO + M^+ + \epsilon_d$  (M = Na, K, Cs) showing the relation of the kinetic energy release  $\epsilon_d$  with the heats of formation of the molecules involved. Thermochemical values are taken from Lias et al.<sup>24</sup> The triangles correspond to peaks in the absorption spectrum of Noda et al.<sup>9</sup> The dashed line indicates direct dissociation. The  $\epsilon_d$ spectrum is the same as in Figure 5.

leads to a modified  $P(\epsilon_d)$  function, which can be fitted to the measured data.

States Populated by Charge Exchange. The small difference in the maximum observed  $\epsilon_d$  values for the three targets suggests that the internal energy of the neutralized acetyl is comparable in all cases. This is supported by the observation that also the maximum of  $P(\epsilon_d)$  occurs at the same  $\epsilon_d$  value for all three targets. This would mean that predominantly the same molecular state is populated regardless of the electron donor. This can be due to the scarceness of suitable electronic states: if few states are available, few neutralization channels exist. An indication of the bound states can be found in the absorption spectrum of Noda et al., which features peaks at 2.30, 2.48, and 3.65 eV.<sup>9</sup> These are indicated by triangles in Figure 8.

Kinetic energies are observed which are larger than the excess energy  $E^*$ . The  $E^*$  values expected from (7) are 1.3, 2.1, and 2.5 eV for the Na, K, and Cs target, respectively, with RE-(CH<sub>3</sub>CO<sup>+</sup>) = 7.0 eV <sup>19,24</sup> and  $E_A$ (CH<sub>3</sub>-CO) = 0.61 eV. The measured kinetic energies reach 2.5, 2.9, and 2.8 eV, respectively. Since  $E_{rev}$  is negligible, the kinetic energy should not be larger than the excess energy. From the shape of  $P(\epsilon_d)$  and the theoretical curves given in (9) and (11) below it is suspected that even higher energies may occur with low intensity. The defect energies are therefore at least 1.2, 0.8, and 0.3 eV, respectively.

High kinetic energies could be due to the creation of highly excited states by charge exchange or to the existence of excited ions in the beam approaching the collision cell. We consider in turn these possibilities. To account for the measured kinetic energies, the state absorbing at 3.65 eV would have to be populated, as can be seen from Figure 8. For K and Na, however, the 2.48- and 2.30 eV-states lie closer to their respective resonance energies. Since no information is available over these states, no argument can be given why they should not be accessible when the ion is neutralized. Internal energy of vibrationally excited ions can be conserved in the nonimpulsive charge-exchange process and could therefore be responsible for the observed high energies. The formation of  $CH_3^+ + CO$ , which is the dissociation channel of  $CH_3CO^+$  with the lowest activation energy, requires 3.57 eV; therefore excited ions could exist in the beam reaching the collision cell. However, the thermal energy of acetyl ions of 450 K is only 0.1 eV, and the internal energy due to the dissociative ionization of acetone should not be very high, either: when 13-eV electrons were used for the production of acetyl cations (which have an appearance energy of 10.53 eV<sup>24</sup>), no change in the maximum kinetic energy release was observed. Thus, there is no unambiguous explanation for the occurrence of the high kinetic energies at the tail of the dissociation.

is an indication that energy scrambling over the internal degrees of freedom is efficient. The states involved are bound long enough to make this possible. Thus the quasi-equilibrium hypothesis seems to hold.

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The difference in the low-energy part of the  $\epsilon_d$  spectra in the  $CH_3CO^+/Na$  and  $CH_3CO^+/Cs$  experiments is probably due to an additional process occurring upon neutralization with Na. This process leads to a continuous  $\epsilon_d$  spectrum at low energies.

From the above arguments we carefully conclude that neutralization of CH<sub>3</sub>CO<sup>+</sup> ions on Cs, K, and Na takes place to the same state of the acetyl radical, leading to the smooth  $\epsilon_d$  spectrum above 0.2 eV.  $CH_3CO^+/Na$  populates additional states. These states, leading to low kinetic energy, have a lifetime long enough to allow energy scrambling. The 1.3-eV shoulder is interpreted as being due to resonant neutralization to a repulsive state.

The results of neutralization experiments reported in the literature<sup>11-15</sup> and mentioned in the Introduction can be compared to our results, provided that the same transition state of the acetyl radical is populated in all cases regardless of the target element. The fact that the kinetic energy release measured in the literature experiments and in the experiments described in this paper is comparable suggests that indeed the same transition state is populated. Then the reported lifetimes ( $\leq 0.5 \ \mu s$ ) should pertain to our measurements, too. This poses an upper limit to the lifetime of the excited molecule, while the fact that energy scrambling is observed points to processes with a lifetime  $\tau$  appreciably longer than a vibrational period (a vibration with 1000 cm<sup>-1</sup> corresponds to  $\tau = 3 \times 10^{-14}$  s).

The energy distribution function  $P(\epsilon_d)$  allows us to draw conclusions about energy redistribution and about structural and dynamical effects in the transition state. As mentioned before, the smoothness of the  $P(\epsilon_d)$  curve means that the available quantum states for the energy to be distributed are closely spaced or quasi continuous. No dissociations occur with very low  $\epsilon_d$  values in the K and Cs experiments in spite of the negligible reverse activation energy  $E_{rev}$ . The onset of the distribution is downshifted for deuterated acetyl. These arguments point to kinematic and dynamical effects in the dissociation. This will be explained in detail below.

Distribution of Kinetic Energy: One-Dimensional. In quasiequilibrium theory, the probability of a process to occur is determined only by the phase-space volume or number of available quantum states. Complete energy scrambling is assumed, justifying the description of the molecular phase space of an isolated molecule by a microcanonical ensemble. The relevant phase spaces are the ones of the ground-state reactant and the transition state. Dynamical constraints of the reaction are not included. From this model, which is successfully used for the calculation of ionic dissociation rate constants, the distribution of kinetic energy  $P(\epsilon_d)$ for a given reactant internal energy E can be calculated in a straightforward manner. This leads to a standard equation for the kinetic energy release in a one-dimensional statistical dissociation.<sup>27,28</sup> For clarity, we will give a derivation below. In this most simple model, the bond in question is assumed to break if the corresponding stretching degree of freedom contains more energy than the activation energy  $E_A$ . Upon dissociation, this extra translational energy  $E_t$  along the one-dimensional reaction coordinate is transformed into fragment kinetic energy. If a barrier  $E_{\rm rev}$  for the reverse reaction exists, it simply leads to a bias in the measured energy.

We separate the degree of freedom that leads to kinetic energy from the remaining S - 1 degrees of freedom. We denote quantities of this stretching bond by the subscript t and quantities of the remaining molecule by the subscript m. Furthermore, we define N(E), the number of quantum states at energy E. The phase space volume  $W^*(E^*,\epsilon_d)$  of the transition state with internal energy up to  $E^*$  and kinetic energy  $\epsilon_d$  is that part of the total

The range of the measured kinetic energy is wide (0.2 to  $\geq 2.5$ eV, not considering the low-energy tail in  $CH_3CO^+/Na$ ). This

<sup>(27)</sup> Franklin, J. L. In Gas Phase Ion Chemistry; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, p 273.

<sup>(28)</sup> Forst, W. Theory of Unimolecular Reactions; Academic Press: New York, 1973.



Figure 9. Theoretical energy distribution functions for the different models. Part A shows the curve described by (9): one (stretching) degree of freedom is converted into kinetic energy. Parts B-D show curves described by (11): two (stretching and bending) degrees of freedom are converted into kinetic energy. In parts B-D the populations  $N_b$  of the bending mode are different. (B):  $N_b$  = constant. (C):  $N_b$  peaked around  $E_b = 0.7 \text{ eV}$ . (D):  $N_b$  peaked around  $E_b = 1.0 \text{ eV}$ . (C) and (D) are the results of a calculation without and with fitting of the parameters  $E_{\rm b}$  and  $\sigma$  and the conversion efficiency (see text). Excess energy  $E^* =$ 3 eV, reverse activation energy  $E_{rev} = 0$ , stretching frequency = 900 cm<sup>-1</sup>, and bending frequency = 500 cm<sup>-1</sup>. In part D a measured spectrum is shown. It is composed from two measurements with long and short flight length, measured with Cs ( $\epsilon_d < 0.8 \text{ eV}$ ) and K ( $\epsilon_d > 0.8 \text{ eV}$ ) as electron donors.

available phase space where these energy conditions are met. Formally, this can be written as

$$W^{*}(E^{*},\epsilon_{d}) = \sum N_{t}(E_{t}) \sum N_{m}(E_{m}) \ \delta(E_{t};\epsilon_{d}-E_{rev}) \ \delta(E_{m};E^{*}-E_{t})$$
(8)

where the  $\delta(x;x')$  are Dirac delta functions ensuring partitioning and conservation of energy. We substitute the discrete sum  $\sum N_t(E_t)$  by the integral over the continuous density of states  $\int dE_t$  $\rho_t(E_t)$ , since the spacing of translational energy levels is of the order of Planck's constant. For polyatomic molecules,  $N_{\rm m}(E_{\rm m})$ is large and therefore the switch from sum to integral is allowed. Due to the  $\delta$  functions, (8) reduces to

$$P(\epsilon_{d}) \propto W^{\dagger}(E^{\dagger}, \epsilon_{d}) \propto \rho_{t}(\epsilon_{d} - E_{rev})\rho_{m}(E^{\dagger} - (\epsilon_{d} - E_{rev})) \propto \{E^{\dagger} + \alpha E^{\dagger}_{z} - (\epsilon_{d} - E_{rev})\}^{S-2}$$
(9)

The density of states  $\rho_t$  disappears from the expression, since the rate of passage through the transition state is independent of  $E_{1,2}^{29}$ Following Whitten and Rabinovitch,  $\rho_m(E^*)$  is approximated by a function proportional to  $\{E^* + \alpha E^*_{\ 2}\}^{S-2}$ . The zero point energy correction  $\alpha E^*_z$  is of importance only at low energy. Equation 9 describes a function that is zero below  $\epsilon_d = E_{rev}$ , rises stepfunction-like to its maximum value, and falls off to higher energies with a power dependence. It is displayed in Figure 9A. Since S-2 usually is a high number,  $P(\epsilon_d)$  drops quickly to very low values, making difficult the determination of the maximum  $\epsilon_d$  value and the internal energy E of the reactant.

There is clear disagreement between the measured kinetic energy spectra and the distribution function derived from simple quasi-equilibrium theory. While the high-energy side of the distribution does show the shape derived from the simple model outlined above, a deviation occurs at the low-energy side, where the predicted stepped intensity rise is not seen. Instead, the measured  $\epsilon_d$  curves show at the low-energy side a smooth rise to their maximum value.

Similar energy distributions have been measured before for neutral and ionic dissociations.<sup>17,32,33</sup> In fact, no distributions have been found that behave according to (9). Several theoretical approaches were published that use refined statistical theories for the calculation of product energy distributions. Conservation of angular momentum is usually the most important factor.<sup>33-36</sup> The

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Figure 10. Schematic picture of the dissociation process  $CH_2CO^{**} \rightarrow$  $CH_3$  + CO. The conversion is shown of skeletal bending energy into CO rotation and orbital angular momentum of the fragments. At large fragment separation, the latter is measured as kinetic energy release. C.M. denotes the center of mass.

result of such phase-space calculations for the dissociation of acetyl radicals into methyl and carbon monoxide has been published by Kroger and Riley.<sup>36</sup> The calculated shape of the kinetic energy distribution function is comparable to the one shown in Figure 5, but the energies involved are too low.

Distribution of Kinetic Energy: Two-Dimensional. To account for the difference between theory and experiment, we have looked in more detail to the dissociation process of acetyl, especially to the consequences of the bent structure of the radical. The different CCO angle of the linear acetyl ion and the bent neutral suggest excitation of the CCO-bending mode (typical energy 500 cm<sup>-1</sup>) upon neutralization. We have used a simple kinematic model (Figure 10) to calculate the effect of skeletal bending energy on the kinetic energy release. The acetyl radical is modeled by a bent triatomic molecule with energy  $E_{\rm b}$  in the CCO-bending motion. The methyl group is represented by a point with mass 15 u. The CCO-bond angle is 120°, the C-O distance is 1.2 Å, and the C-C distance is 1.5 Å.

When in the transition state the bond between the two carbon atoms is broken, the bending motion causes rotation of the CO fragment. As the total angular momentum is conserved, the rotational angular momentum vector of the CO has to be counterbalanced by the orbital angular momentum between the two fragments CH<sub>3</sub><sup>•</sup> and CO. The energy in the radial motion is asymptotically converted to kinetic energy. Finally a small part of the energy in the bending mode is directly converted to radial energy of the separating fragments. Application of the conservation laws shows that the ratio between the kinetic energy of the fragments over the rotational energy of the CO molecule is 3/2, so  $0.6E_b$  is converted into kinetic energy. This ratio is dominated by the ratio of the moments of inertia  $I = \mu_{12} R_{12}^2$  of the fragment pair  $CH_3^{\bullet} + CO (I = 22 \text{ u } \text{Å}^2)$  on the one hand and the CO molecule  $(I = 15 \text{ u } \text{Å}^2)$  on the other.

We implement this conversion of bending energy to kinetic energy into the statistical formalism outlined above. The dissociation process can be considered as two-dimensional, since we now include an additional degree of freedom. We assume that the two contributions to the kinetic energy can simply be added:  $\epsilon_{\rm d} = E_{\rm t} + 0.6E_{\rm b} + E_{\rm rev}$ . The phase-space volume of the transition state is then

$$W^{*}(E^{*},\epsilon_{d}) = \sum N_{b}(E_{b}) \sum N_{t}(E_{t}) \sum N_{m}(E_{m}) \times \delta(E_{t};\epsilon_{d}-E_{rev}-0.6E_{b}) \delta(E_{m};E^{*}-E_{t}-E_{b})$$
(10)

Again, we substitute the sums over  $E_t$  and  $E_m$  by integrals and find

$$P(\epsilon_{\rm d}) \propto \sum_{E_{\rm b}} N_{\rm b}(E_{\rm b}) \ \rho_{\rm t}(\epsilon_{\rm d} - E_{\rm rev} - 0.6E_{\rm b}) \ \rho_{\rm m}(E^{*} - (\epsilon_{\rm d} - E_{\rm rev}) - 0.4E_{\rm b})$$
(11)

The sum over  $E_b$  is not replaced by an integral, because  $N_b$  is not large enough to validate the continuous approximation. The lower and upper sum limits are, respectively,  $E_b = 0$  and  $E_b = (\epsilon_d - E_{rev})/0.6$  or  $E^*$ , whichever is lower. In Figure 9B we show  $P(\epsilon_d)$ calculated according to (11). The bending mode is assumed to

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Figure 11. Simulated "neutral mass spectrum" of the two-step reaction  $CH_3CO^{\bullet\bullet} \rightarrow CH_3^{\bullet\bullet} + CO + 1 \text{ eV} \rightarrow CH_2 + H^{\bullet} + CO + 0.01 \text{ eV}$ . The small spikes at the high mass side of the mass peak are due to nonrandom sampling of the dissociation angle  $\Theta$ .

exchange energy with the rest of the molecule. The expected smooth rise at the low-energy side is seen, but the position of the maximum lies at too low  $\epsilon_d$  values.

There are several possibilities conceivable to account for the observed maximum position of the energy distribution function. One is that more than two internal degrees of freedom contribute to the kinetic energy release. This would enlarge the phase space which corresponds to larger fragment translational energies. The other possibility is that the skeletal bending energy is not exchanged efficiently with the energy in the other vibrational modes, which is in contrast with the quasi-equilibrium assumption. This "isolated" energy changes the statistical weight of the individual bending levels. This is mirrored by the kinetic energy distribution function. We discard the first proposal because there are no more internal molecular motions that can be converted efficiently to fragment translation. The second proposal is supported by the argument that the CCO-bending mode is by far the lowest frequency mode of the molecule and therefore energy exchange during the lifetime of the excited molecule can be inefficient. To estimate  $E_b$ , we have approximated the bending potential of acetyl by the literature bending potential of CH<sub>3</sub>CN<sup>38</sup> and find  $E_{\rm b}$  = 0.67 eV for an angle that deviates  $60^{\circ}$  from the equilibrium angle.  $N_{\rm b}$  is approximated by the Franck–Condon factors for the population of the bending levels, calculated according to Gislason et al. If only the v = 0 upper state is considered, the vibrational distribution is a Poisson distribution.<sup>39</sup> The use of this vibrational population leads to the energy distribution function which is shown in Figure 9C. The fit is satisfying for such a rough model, but still the peak width is too small and its maximum occurs at too low energies. The average value and width of the population of the vibrational levels in the isolated bond, scaled with the conversion efficiency to kinetic energy, are imaged in the position and width of  $P(\epsilon_d)$ . Another factor that strongly influences the slope of the high-energy side of the energy distribution is the effective number  $\sigma$  of degrees of freedom. This concept has been used before in rate constant calculations.<sup>40,41</sup> Since it is an appealingly simple parameter, we use it for the interpretation of our measurements. It has been used, for example, for discerning direct cleavages from rearrangement dissociations in neutralized cyclohexane. For a more detailed discussion, we refer to our previous paper.<sup>17</sup> As in the case of cyclohexane, we found that  $\sigma$  is much less than the theoretical number (S - 2). A good spectrum reconstruction was obtained with the following parameters:  $\sigma = 7$ ,  $E_{\rm b} = 1$  eV, conversion efficiency 0.7. This spectrum is compared to a measured spectrum in Figure 9D. In our opinion, the excellent match indicates strongly that the dissociation of acetyl is not purely governed by energy scrambling as presupposed by the statistical hypothesis. In the dissociation behavior several deviations from it may be reflected: (i) selective excitation of the bending mode due to the geometry change uppon neutralization; (ii) inefficient internal coupling of the low-frequency bending mode to the rest of the molecule; (iii) incomplete energy scrambling in the same part of the molecule.

The shift in the distributions  $P(\epsilon_d)$  of CD<sub>3</sub>CO and CH<sub>3</sub>CO (Figure 6B,C) can be estimated from the ratio of the moments of inertia of the pairs CH<sub>3</sub> + CO and CD<sub>3</sub> + CO, which is  $I(CH_3-CO)/I(CD_3-CO) = 0.89$ . This would lead to a downshift in the distribution of about 11%, which corresponds satisfyingly with the measured shift by 0.1 eV.

The observed raised base line at the low mass side of the discrete peaks is due to multiple dissociations. Since the detector is tailored for the detection of two coincident particles, such processes would lead to erroneous data points in spectra. Simulations have been performed, assuming two subsequent dissociations of a precursor molecule to form three particles. Both dissociations have been assumed to be isotropic. The observed spectra are consistent with secondary dissociations of low-energy release yielding light particles. In Figure 11 we show the result of a simulation of the reaction  $CH_3CO \rightarrow CH_3 + CO \rightarrow CH_2 + H + CO$ .

### Conclusion

Translational spectroscopy in combination with dissociative charge exchange has been employed for the study of dissociative mechanisms of small polyatomic molecules. The selected molecules  $CH_3Cl$  and  $CH_3CO^{\bullet}$  show completely different dissociation behavior: the mechanism in methyl chloride is direct dissociation via a repulsive surface, while the dissociation of the acetyl radical is preceded by statistical scrambling of the internal energy. The kinetic energy release distribution in the dissociation of  $CH_3CO^{\bullet}$ shows that the process is statistical. The low-energy part of the distribution is consistent with structural and dynamical effects: selective excitation of weakly coupled bending modes appears to be crucial for the amount of internal energy that is converted into fragment kinetic energy.

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**Registry No.**  $CH_3Cl^{++}$ , 12538-71-5; Na, 7440-23-5;  $CH_3Cl$ , 74-87-3; K, 7440-09-7; Cs, 7440-46-2;  $CH_3CO^+$ , 15762-07-9;  $CH_3CO^{+}$ , 3170-69-2.

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