

Model-Free Determination of Dissociation Energies of Polyatomic Systems

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We describe and apply a new procedure that allows a direct determination of dissociation energies of polyatomic systems (clusters, fullerenes, polymers, and other molecules) without any modeling of the systems under investigation. As an example, we have determined the dissociation energies of a series of gold clusters Au_n^+ . A comparison with values obtained from statistical models of unimolecular dissociation shows that these models significantly fail to describe the data. In contrast, the new method yields values which are an order of magnitude more accurate, thus allowing one to experimentally set benchmarks for any theory which attempts to describe activated processes.

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The most fundamental parameter of any disintegration process of a free stable polyatomic particle is the dissociation energy, i.e., the minimum excitation energy necessary to induce the decay. In the case of unimolecular reactions the observed decay processes frequently occur delayed and via an activated process which leaves the product in a state with an unknown amount of excitation energy. Even when the initial excitation energy is known, the dissociation energy can be found only by modeling the decay, e.g., by equating measured rates to one of the available theoretical expressions for rate constants [1–8]. However, such a determination of the dissociation energies is rather indirect and depends on the characteristics of the respective model as well as a number of often implicit assumptions concerning the thermal properties of the systems. In the following, we describe and apply a procedure that allows a direct measurement of dissociation energies, i.e., without any assumptions on how the decay proceeds. As an example, we have determined the dissociation energies of a series of gold clusters Au_n^+ . For comparison, the dissociation energies have been determined from the observed decay rates by application of transition state theories [4–6], detailed balance approaches [3,7,8], or Arrhenius plots.

The basic idea of the new method is to compare the excitation energy E_A of a sequential decay



with the corresponding energy E_B of the single decay



leading to the same final product. When the single decay process (2) depends in a measurable way on the amount of excitation energy present, e.g., through the decay rate, it can be used as an uncalibrated thermometer for the last step of the sequential reaction (1). Adjusting either of the two excitation energies E_A and E_B to produce the same reading of the thermometer, the difference in excitation energies, $E_A - E_B$, is a direct measure of the energy consumed in

the first step of the sequential decay, which is essentially the dissociation energy of A .

We have applied this method to gold cluster ions Au_n^+ consisting of $n = 14$ to 24 atoms. The ions were produced in a laser vaporization source [9,10], transferred to a Penning trap [11–13], and mass selected; i.e., for each measurement the cluster size of interest was isolated. Inert gas was used to center the clusters in the trap. Thermalization to room temperature was checked by varying the average pressure in the trap from 3×10^{-5} Pa to 8×10^{-4} Pa amounting to a number of some ten to some hundred collisions with the argon atoms. No change in decay rates was observed, indicating that the helium pulse used in the cluster source [10] is sufficient for thermalization.

The mass selected clusters were photoexcited by a nanosecond dye-laser pulse with photon energies between 2 and 6 eV. At appropriate excitation energies, delayed dissociation can be observed in a time-resolved fashion with decay times in the range from ten microseconds to several tens of milliseconds [14]. To this end, the clusters are kept stored in the trap for a variable time between photoexcitation and product analysis. The latter is performed by time-of-flight mass spectrometry, i.e., ejection of all charged particles from the trap into a drift tube and single ion counting of both the precursor and fragment ions [11,12].

For the present case the sequential process is $\text{Au}_n^+ \rightarrow \text{Au}_{n-1}^+ + \text{Au} \rightarrow \text{Au}_{n-2}^+ + 2\text{Au}$, and the thermometer process is $\text{Au}_{n-1}^+ \rightarrow \text{Au}_{n-2}^+ + \text{Au}$. The Au_n^+ clusters of the size range investigated are known to decay by evaporation of single neutral atoms [15]. In the case of Au_{15}^+ which also evaporates neutral dimers [15], the partial monomer decay rate was used for the analysis. The time evolutions of the relative fragment yields are well represented by a single exponential from which the decay rate is determined. In the sequential decays the first process is so rapid that the lifetime of the intermediate can be determined unambiguously. With total initial excitation energies of E_n and E_{n-1} for the sequential and the thermometer processes, respectively, the absolute dissociation energy of Au_n^+ is

obtained as

$$D_n = E_n - E_{n-1} - E_{\text{KER}}. \quad (3)$$

The term E_{KER} accounts for the small part of the initial excitation energy E_n which is carried away as translational kinetic energy of the departing fragments of the primary process (KER for kinetic energy release) and therefore lost for the thermometer process. The energies E_n are given by the sum of the photoexcitation energy and the small initial room temperature thermal energy

$$E_n = E_{\text{ph},n} + E_{\text{th},n}. \quad (4)$$

Thus, Eq. (3) can be written as

$$D_n = E_{\text{ph},n} - E_{\text{ph},n-1} + (E_{\text{th},n} - E_{\text{th},n-1}) - E_{\text{KER}}. \quad (5)$$

The contributions of both the thermal energy and the KER lead to only small corrections. The thermal energy is given by approximately 0.021 eV per vibrational degree of freedom, as calculated from the bulk heat capacities. A Debye approach results in the very similar value of 0.020 eV. Thus, the difference in thermal energies of the precursors in the sequential process and the thermometer process can be estimated to $\Delta E_{\text{th}} = E_{\text{th},n} - E_{\text{th},n-1} = 0.063$ eV. The kinetic energy release is a measurable quantity [16–18], but in view of the small magnitude of the correction, a calculated estimate suffices here. A harmonic oscillator parametrization of the density of states and one of three models, the empirical Haney parametrization [19], a detailed-balance calculation [7] based on the geometrical capture cross section, or one where the polarizability is taken into account [8], all yield values of the order of 0.1 eV and differ less than 0.029 eV from each other for any present cluster size and excitation energy; i.e., the systematic uncertainty is about 2 orders of magnitude smaller than the measured shift in photoexcitation energy, $E_{\text{ph},n} - E_{\text{ph},n-1}$. As generally assumed for clusters [20] and experimentally verified, e.g., for sodium clusters [21], no reverse reaction barrier is added to the KER. However, the present method can easily be accommodated to reactions with barriers if experimental KER values should show otherwise.

As an example, Fig. 1 shows the observed decay rates of Au_{16}^+ as a function of the photoexcitation energy for both the direct process $\text{Au}_{16}^+ \rightarrow \text{Au}_{15}^+$ and the sequential decay $\text{Au}_{17}^+ \rightarrow \text{Au}_{16}^+ \rightarrow \text{Au}_{15}^+$. While the decay of Au_{16}^+ is induced by absorption of a single photon, the sequential decay process of Au_{17}^+ is initiated by absorption of two photons. The absolute number of absorbed photons is known from consistency checks, i.e., a different assignment of photon numbers would lead to unreasonable values of the dissociation energy. The difference between the number of absorbed photons for the direct decay and for the sequential

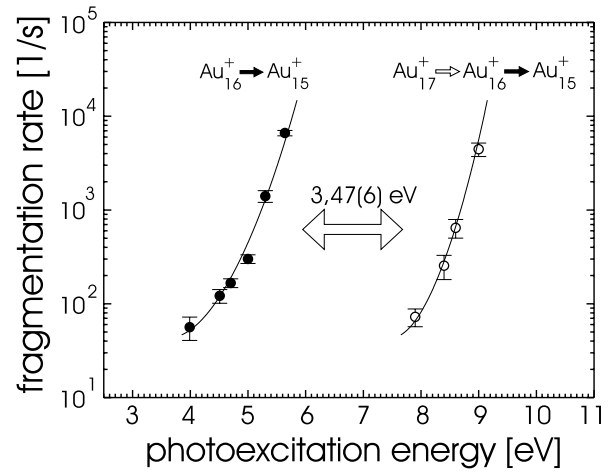


FIG. 1. Rates of the unimolecular dissociation $\text{Au}_{16}^+ \rightarrow \text{Au}_{15}^+$ as a function of photoexcitation energy for mass selected Au_{16}^+ clusters (full symbols) and for sequential decays of mass selected Au_{17}^+ clusters (open symbols). The lines through the data are drawn to guide the eye.

decay is known unambiguously since an incorrect assignment would lead to different slopes of the two curves in Fig. 1. A fraction of clusters absorb a different number of photons, but this causes no problem for the analysis since it changes only the background level of the time-resolved decay curves and not the decay constant. This has been checked by varying the laser fluence in a number of cases. Only the yield changed, not the time constants, indicating that absorption of an extra photon pushes the rate constant above the experimental time window. This observation is confirmed by numerical estimates of rate constants which give large differences between rates for 2 and 3 (or 3 and 4) absorbed photons.

As shown in Fig. 1 there is a constant energy shift between direct and sequential decay independent of the decay rate under consideration. The displacement of the curves by $E_{\text{ph},17} - E_{\text{ph},16} = 3.47(6)$ eV corresponds to the dissociation energy of Au_{17}^+ given by $D_{17} = E_{\text{ph},17} - E_{\text{ph},16} + \Delta E_{\text{th}} - E_{\text{KER}}$. The resulting value for the dissociation energy of Au_{17}^+ is 3.37(9) eV, where the uncertainty is mainly of statistical nature. The values thus obtained allow an absolute check of other, more conventional but less direct, methods to extract unimolecular activation energies from energy resolved rate constants. With the data from the measurements of the thermometer process the decays were analyzed with Arrhenius plots and by a number of expressions which relate decay constants, excitation energies, and activation energies. As an example, Fig. 2 shows Arrhenius plots for the decays of $\text{Au}_{17}^+ \rightarrow \text{Au}_{16}^+$ and $\text{Au}_{18}^+ \rightarrow \text{Au}_{17}^+$.

The necessary conversion from energy to an effective temperature for the decay process was accomplished by subtracting $D_{17}/2$ and $D_{18}/2$, respectively, from the excitation energy and dividing by the microcanonical heat capacity $(3n - 7)k_B$ [22,23].

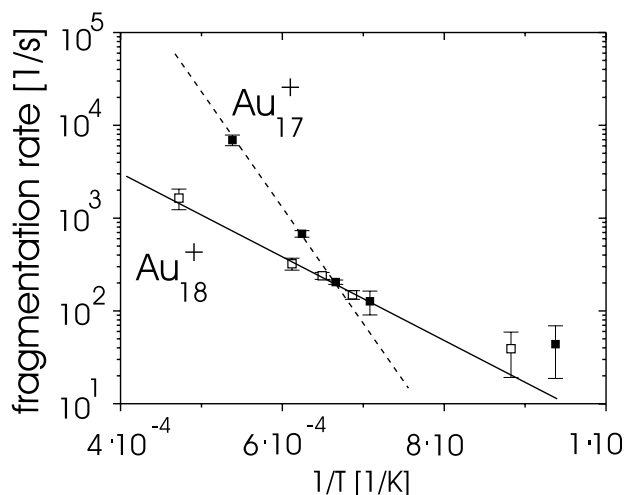


FIG. 2. Decay rates of mass selected photoexcited Au_{17}^+ (full squares) and Au_{18}^+ clusters (open squares) as a function of the inverse temperature in a pseudo-Arrhenius plot. The Arrhenius fits of Au_{17}^+ and Au_{18}^+ are indicated by a dashed line and a solid line, respectively. The definition of T is discussed in the text.

The activation energies extracted from a straight-line fit to the data, 2.27(0.20) eV for Au_{17}^+ and 0.95(0.03) eV for Au_{18}^+ are significantly lower than the model-free values. Several alternative effective temperatures can be defined but no *a priori* justified version has been found which gives a general agreement between the model-free and the Arrhenius dissociation energies. For the case of Au_{16}^+ this is already clear from the positive curvature of the curves shown in Fig. 1. This translates into a strong positive curvature similar to the one seen in Fig. 2 for Au_{17}^+ . Barring pathological transition states, any model for an activated process based on harmonic oscillator densities of state has a negative curvature.

The Arrhenius plots for most clusters investigated were found to suffer from a positive curvature, similar to Au_{17}^+ . A few, as in the case of Au_{18}^+ , are straight lines as expected, but with a slope which corresponds to less than half the true value of the activation energy. Such cases are particularly problematic for a traditional analysis since there is no inherent indication that they fail. Also, the fitted frequency factors (e.g., 2.0×10^{10} Hz for Au_{17}^+ and 3.2×10^5 Hz for Au_{18}^+) are much lower than the expected values. Frequency factors are model dependent but are in no case less than the Debye frequency for gold (3.5×10^{12} Hz) [24].

A related problem is encountered for the standard procedures to connect the rate constants to dissociation energies. As Fig. 3 shows, the inversion of measured rate constants by use of either RRK (Rice-Ramsperger-Kassel) [1], QRRK (Quantum-RRK) [2], RRKM (RRK-Marcus) [4–6], Engelking [7], or Weisskopf [3,8] formulas yield the unsatisfactory result that the fitted value of the dissociation energy depends significantly on the excitation energy at which it has been measured. This holds for different level density expressions [25,26] that have been employed

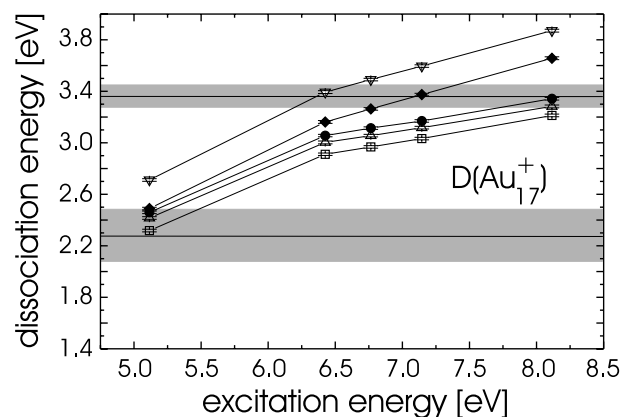


FIG. 3. Calculated dissociation energy of Au_{17}^+ as deduced from the observed decay rates by the use of various techniques (see text) at several excitation energies (same data as in Fig. 2). For comparison the values of the determination by comparison of sequential and direct decays (upper line, data of Fig. 1) and the Arrhenius value (lower line, data from Fig. 2) have been included. Shaded areas indicate 1σ error bars.

in the RRKM and Weisskopf approaches and for different frequency distributions employed in the Engelking approach, from a Debye-like distribution to more elaborate types [27]. The Weisskopf formula was used with values extrapolated from bulk properties [28], both with and without inclusion of melting which occurs at 1336 K in the bulk [24].

This defect is a general one and not limited to Au_{17}^+ or Au_{18}^+ . The variation of D with energy can be parametrized by the derivative $(3n - 6)dD_n/dE_n$. A perfect description of the data by these models would correspond to the value zero, i.e., no change of the determined dissociation energy as a function of the excitation energy. For the worst case of a complete insensitivity of the rate constant to the energy the value would be around 25. For the Au_n^+ dissociation energies, $n = 14$ –24, fitted by RRKM and Weisskopf calculations, the resulting values range from 2 up to 16. Figure 4 shows the dissociation energies of the clusters Au_n^+ ($n = 14$ –24) for which decay constants of single decays and sequential dissociations have been measured. The plot includes the values from the delayed sequential decays as well as those calculated from the single decays with either the Arrhenius approach or RRKM and Weisskopf expressions. The span of values for the latter two is indicated by a vertical line and has values exceeding 1 eV which translate into systematic uncertainties of these models of more than 30%.

There are two possible explanations for the failure of Arrhenius plots and of rate constant models. One is that the caloric curve could significantly deviate from the harmonic oscillator model or from the values extrapolated from bulk behavior. Obviously, melting could play an important role in this connection. Alternatively, it could be caused by radiative cooling of the clusters in the second, time-resolved, evaporation step. Extrapolation of the radiation

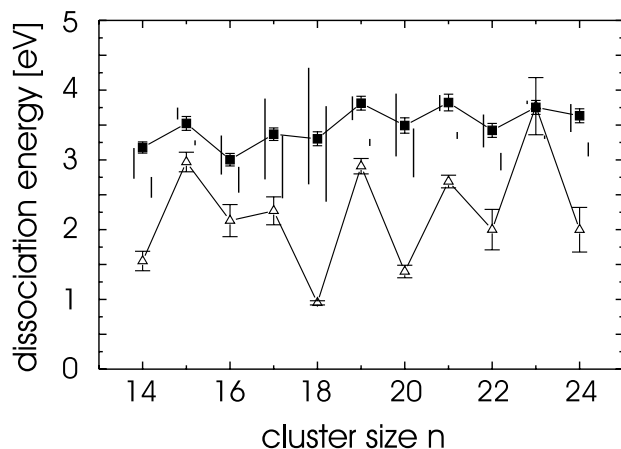


FIG. 4. Dissociation energies of Au_n^+ as a function of cluster size as determined by time-resolved photodissociation. The model-free values are given by full squares and the values from Arrhenius plots by open triangles. Vertical lines to the left and right of the data points indicate the range of dissociation energy values from the Weisskopf expression and the RRKM approach, respectively.

intensity [28] from bulk suggests that this is not the case by a margin of several orders of magnitude. However, with the present knowledge it is not possible to completely rule out this explanation. Both of these effects could cause the observed flattening of the Arrhenius curve.

We have presented a new method for the determination of dissociation energies of polyatomic systems. By a combination of observations of sequential and single-step dissociations, model dependencies and thus systematic uncertainties can be avoided. In the present case the accuracy of the resulting dissociation energies is thereby increased by 1 order of magnitude. While the method has been applied to small gold clusters, it is not restricted to metal clusters and can be extended to the dissociation of systems with reverse barriers, i.e., higher-lying transition states. Furthermore, the method has been presented with time resolved data in the form of exponential decays, but with the only requirement that it is sensitive to internal energy, the thermometer process can be of far more general nature.

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