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The influence of internal degrees of freedom on the unimolecular decay of the molecule–cluster compound $Au_8^+CH_3OH$

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Time-resolved photodissociation measurements of the sequential reaction $Au_8^+CH_3OH \rightarrow Au_8^+ \rightarrow Au_7^+$ and the direct reaction $Au_8^+ \rightarrow Au_7^+$ have been performed for several excitation energies. The production rates and yields of the final state Au_7^+ in the sequential process are strongly influenced by the excitation energy deposited into the evaporated methanol molecule during the initial fragmentation step. Both the rate constants and yields can be fitted with a single parameter, the cluster–methanol binding energy. © *2002 American Institute of Physics.*

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I. INTRODUCTION

Gold was one of the first materials to be studied in connection with cluster formation[1–4] and gold clusters have remained a subject of interest since then. Part of the reason for this has been the desire to explore the similarities between the simple alkali metals and the noble metals in phenomena such as shell structure and odd-even effects in the electronic spectrum. In parallel, gold clusters have found applications as tracers in biological molecules[5] and as substrates for molecule-specific adsorption, as well as potential use as catalysts[6,7] and in nanoelectronics components.

A number of these applications involve bonds between clusters and organic or other nonmetallic molecules. In simple terms this involves the bonding between a molecule that is characterized by well-defined bond lengths and directions and a cluster that can to a similar approximation be described by a spherical mean field potential for the valence electrons. The situation is complicated by deviations from such a jellium[8] behavior of the cluster and it remains a demanding task to obtain reliable theoretical estimates for the properties of such a complex.

In a recent set of studies, spectroscopic changes in methanol due to adsorption to gold clusters Au_n^+ have been observed[9–11] and compared to model calculations.[9,12] It was found that the presence of the cluster ion modifies the properties of the molecule in several ways. The C–O stretching frequency is shifted by a few percent, depending on the cluster size.[10,11] The theoretical frequency shifts were found to be in good agreement with the experimental values. Also, the transition in cluster shape from planar to three-dimensional (3-D) geometry which is predicted between size $n=7$ and $n=8$ is confirmed by the observed frequency shifts.[9] While the cluster geometry is found to depend on the clusters' size, it changes only marginally upon adduct formation, i.e., under the influence of the adsorbed methanol molecule. Likewise, the frequency shifts observed for the internal methanol resonances are relatively small.[10,11] Overall, these minor changes in both the constituents suggest that the cluster–molecule composite is formed by the two intact species and that their internal structure is affected only to a small extent by the weak bonding force.

In the present work we examine the decay dynamics of the complex and the binding energy of the methanol to the cluster by measuring unimolecular decay rates of the excited complex and the quantum yield of the final product. Specifically, the decay chain,

$$Au_8^+CH_3OH \rightarrow Au_8^+ + CH_3OH \rightarrow Au_7^+ + Au + CH_3OH, \tag{1}$$

and the simple decay,

$$Au_8^+ \rightarrow Au_7^+ + Au, \tag{2}$$

were measured time resolved at different excitation energies and their rate constants were compared. The neutral methanol fragment was not detected but considering the nature of the bondings involved there can be little doubt that reaction (1) is the lowest-energy channel.

Traditional methods used to describe unimolecular decays require some amount of modeling and assumptions

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[a)] Electronic mail: manuel.vogel@uni-mainz.de about the system in order to apply one of the many available statistical decay rate theories to, e.g., extract the binding energy from measured decay rate constants. However, as was shown recently,[13] the results thus obtained can be susceptible to serious errors due to effects that have not yet been identified with certainty. While these problems may not be present for the very well-characterized methanol molecule, they are present for the gold cluster,[13] and it is likely that this uncertainty is compounded for the methanol–cluster complex. A complication added by the methanol molecule is the uncertainty about the transition state in the fragmentation process. Even if the ground state of the compound is assumed to be known and to be identical to the theoretically predicted one where the molecule and the cluster are bound by a single bond, it is not possible to infer that the transition state corresponds to the breaking of this bond. In fact, data presented below on the inverse process, the formation of the compound, suggest that this is actually not the case.

These obstacles are to some extent circumvented by a recently developed method to determine the dissociation energies of polyatomic molecules or clusters:[13,14] The method is based on a measurement of the sequential dissociation process of the form $A \rightarrow B \rightarrow C$, which is compared to the single-step process $B \rightarrow C$. The main difference to the present work is that here both fragments of the initial decay (the methanol and the gold cluster) contain a finite number of degrees of freedom. This prevents a direct application of the method. However, since only the energy content of the asymptotically separated fragments is relevant and since the thermal properties of gas phase methanol are well known, it is nevertheless possible to extract valuable information with only a modest amount of modeling.

The details of the method and the experimental procedure are described in Sec. II. After a presentation of the data, the necessary modifications of the method[13,14] are developed and applied in Sec. III.

II. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup and procedure have already been described in detail elsewhere.[15–17] Briefly, the experimental sequence is as follows: The cluster ions are produced in a Smalley-type laser vaporization source,[18,19] and transferred to a Penning trap,[20,16,21] where they are stored. The relevant cluster size is selected by resonant ejection of all other clusters. The methanol is introduced into the trapping region through a pulsed valve and forms complexes with the clusters by soft collisions inside the trap.[22] Methanol adsorption occurs with a high efficiency, i.e., nearly all clusters adsorb one or two methanol molecules. The $Au_8^+CH_3OH$ ion ensemble is mass selected, radially centered, and thermalized inside the trap by use of argon gas.[23]

The complex is then photoexcited by a single pulse from a Nd:YAG-pumped dye laser at a wavelength between 295 and 357 nm, produced by frequency doubling with a BBO crystal. The ion distribution that results from laser irradiation is monitored by ejection from the trap into a time-of-flight (TOF) mass spectrometer with single-ion counting.[15,16] By variation of the storage period between photoexcitation and ejection in the range from a few microseconds to 60 ms, it is possible to follow the delayed dissociation processes time resolved.[24]

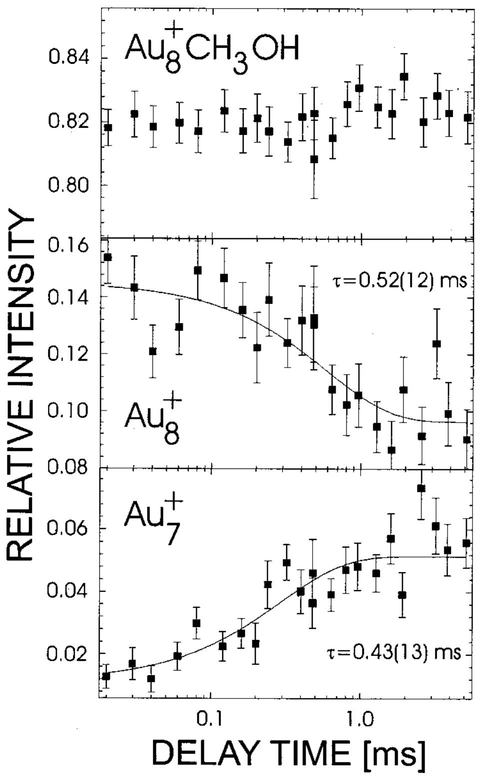

FIG. 1. Relative intensities as a function of the delay period between photoexcitation and detection. The example shows the sequential reaction $Au_8^+CH_3OH \rightarrow Au_8^+ \rightarrow Au_7^+$ of stored $Au_8^+CH_3OH$ after excitation with a 10 ns laser pulse at 3.60 eV photon energy and a pulse energy of 150 μJ. Both precursor and product ions remain stored simultaneously for the chosen delay period. The first reaction step $Au_8^+CH_3OH \rightarrow Au_8^+$ is very fast and outside the experimental time window and the buildup of Au_8^+ is therefore not observed time resolved. The reaction $Au_8^+ \rightarrow Au_7^+$ takes place on the time scale of the experiment and the respective time constants for Au_8^+ decay and Au_7^+ buildup agree.

As an example of a measurement series, Fig. 1 shows the relative intensities of the precursor and the product ions for the sequential dissociation of $Au_8^+CH_3OH$. In this particular case, about 18% of the adduct ions have absorbed a photon and undergone dissociation by spontaneous evaporation of the adsorbed methanol molecule. The excitation energies used have been selected to allow time-resolved observation of the decay of the remaining Au_8^+ clusters to Au_7^+ by neutral monomer evaporation,[25] with decay times on the order of several hundred microseconds.

In addition to the decay time of the Au_8^+, the baseline of the intensity of Au_8^+ (the middle frame of Fig. 1) also provides experimental information on the nature of the decay. Since the Au_8^+ clusters have been produced by single-photon dissociation of $Au_8^+CH_3OH$, a simple exponential decay would involve all clusters and thus no additional baseline is expected. Therefore, even without detailed modeling it is clear from this finite offset that the ensemble of Au_8^+ clusters produced in the first step of the sequential decay cannot be described by a single decay constant. In other words, the energy removed by the evaporated methanol must be de-

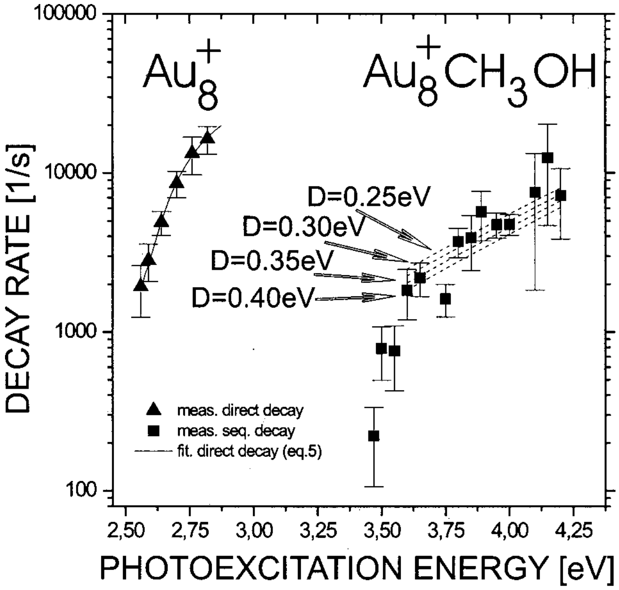

FIG. 2. Rates of evaporation as a function of the excitation energy in direct and sequential dissociation processes leading to Au_7^+ as a final state.

scribed by a distribution with finite width. This will, in general, give a nonexponential behavior, but for practical reasons the time dependence of the respective cluster intensities has been fitted with an exponential function and a baseline. For simplicity of notation, we will write "rate constants" instead of "fitted apparent rate constants" for sequential decays. The resulting decay time for the data in Fig. 1 is about 0.5 ms. The observed time constants of Au_8^+ dissociation and of Au_7^+ buildup agree within statistical uncertainties and provide a check of the assigned pathways.[25]

Similarly, the single-step decay of bare Au_8^+ clusters has been monitored time resolved. For these measurements several different wavelengths ranging from 439 to 484 nm have been used. This yields decay rate constants between 50 and 500 μs.

III. RESULTS AND DISCUSSION

A. Experimental results

Figure 2 shows the experimentally observed monomer evaporation rate constants as a function of excitation energy for the direct process $Au_8^+ \rightarrow Au_7^+$ (full triangles) and the sequential process $Au_8^+CH_3OH \rightarrow Au_8^+ \rightarrow Au_7^+$ (full squares). The measured decay rate constants for the decay of the bare gold clusters (full triangles) show the behavior expected from unimolecular decay theory, i.e., a rate that increases with excitation energy and a negative curvature of the logarithm of the rate constant as a function of excitation energy. The measured rate constants for the gold cluster decaying after methanol has been detached from the initial methanol–cluster compound (full squares) are shifted by 1 eV and more to higher excitation energies with respect to the bare Au_8^+ cluster. It is also clear from the figure that this shift is not constant; the slope of the $Au_8^+CH_3OH$ curve is reduced compared to the decay of the bare gold cluster. As a first approximation one can calculate the shift as follows: At a typical decay rate constant of $k = 4 \times 10^3\ s^{-1}$, say, the shift is $E_s = 1.3$ eV. From the photoexcitation energy at that decay constant, $E_{ph} = 2.62$ eV, and the harmonic oscillator heat capacity an equivalent temperature (in units of k_B) of $E_{ph}/C_v + 300\ K = 0.105$ eV is calculated. With the known vibrational frequencies of methanol,[26] the vibrational energy content of the methanol molecule at that temperature is found to be $E_{Me} = 0.60$ eV. The translational and rotational energy of the methanol at that temperature is given by $E_{tr,rot} = (2 + \frac{3}{2}) \times 0.105\ eV = 0.37$ eV. The difference between the experimentally observed energy shift E_s and the energy the methanol molecule removes during dissociation is given by $E_s - E_{Me} - E_{rot,tr} = 0.3$ eV. This number represents a first estimate of the dissociation energy of methanol from the compound. However, other choices of the reference rate constant than $k = 4 \times 10^3\ s^{-1}$ give different values and the above value can therefore only be considered a first approximation.

B. Data simulation and fitting

The analysis can be improved if we consider the finite width of the distribution of excitation energies left in the cluster after evaporation of the methanol. As already mentioned, the partition of the energy between the gold cluster and the methanol is not sharp. Given the limited number of degrees of freedom and hence the small heat capacity of both the cluster and the molecule, the fluctuations around the mean are relatively large. Hence, even for well-defined initial excitation energies of the complex $Au_8^+CH_3OH$, the excitation energy of the product Au_8^+ is not well defined. This aspect is essential for the quantitative interpretation of the data since the decay of the product is very strongly energy dependent. A sufficiently broad energy distribution will lead to a scale-invariant decay curve that varies as $1/t$.[27] The present case is intermediate between a sharp and a completely smeared energy distribution. This causes a reduction of the slope of the curve for the $Au_8^+CH_3OH$ data in Fig. 2. It also means that the measured rates not only depend on the initial excitation energy but also on the precise measurement time window. It is therefore necessary to calculate the yields at the same delay times as the experimental data are measured. We have adopted this procedure in the following numerical simulation of the data.

The distribution of excitation energies of the Au_8^+ clusters after the methanol molecule has been evaporated is given by the statistical weights of the two products. For the cluster we use the bulk caloric curve extrapolated to $n = 8$,[28] which is fairly close to the harmonic oscillator value. The level density of the methanol is calculated from the vibrational frequencies. The contribution from the rotational and translational degrees of freedom is not negligible. We represent the level density of these degrees of freedom by a power law with a power of $\frac{5}{2}$. This power is compounded by a power of $\frac{1}{2}$, which corresponds to unrestricted rotation of the methanol molecule in the transition state, a power of 1 in the geometric capture cross section[29] and a power of 1 in the convolution of these two contributions [see Eq. (3)]. This corresponds to a transition state that is the asymptotically separated configuration.

Some information on the nature of the transition state is available from measurements of the methanol–cluster reaction rate in the trap. With a methanol pressure of about 5×10^{-7} mbar, an interaction time of 150 ms and a total yield of about 90%, the cluster–methanol capture cross section is a few hundred Å^2. This value is somewhat uncertain, mainly because of the uncertainties connected with the methanol pressure. Nevertheless, it indicates a capture cross section on the order of the geometric value. Thus, it also corroborates the suggestion that no reverse activation barrier is present and that the activation energy for the process is identical to the dissociation energy.

The distribution of internal energies of the cluster after methanol evaporation is then given by

$$p(E_{\rm cl})\propto\int_0^{E_{\rm tot}-D}\rho_{\rm cl}(E_{\rm tot}-D-E_{\rm Me})\times\int_0^{E_{\rm Me}}\epsilon^{5/2}\rho_{\rm Me}(E_{\rm Me}-\epsilon)d\epsilon\, dE_{\rm Me}. \qquad (3)$$

The internal energy left in the cluster is denoted by $E_{\rm cl}$, the total initial energy by $E_{\rm tot}$, and the methanol–cluster dissociation energy by D. The function $p(E_{\rm cl})$ is peaked at a value of roughly $C_{v,\rm cl}/(C_{v,\rm cl}+C_{v,\rm Me})$ but has a significant width. The contribution to the width of the Au_8^+ energy distribution from the room temperature width of the cluster–molecule complex is relatively small when these are added in square. The change in the total width is only about 9% for the typical energy of 2.7 eV and for computational simplicity it has been ignored in the further analysis. For each test value of D (0.20 eV, 0.25 eV,...,0.60 eV) for which D has been tested, the internal energy distribution of the cluster is calculated and converted to rate constants with the help of the measured, energy-resolved, rate constants for the bare gold clusters shown in Fig. 2 (see below for a description of the parametrization of this rate constant). The remaining Au_8^+ yield $I_{\rm sim}$ after a delay time t_i is then simulated by averaging over all disintegration rates with the calculated weight:

$$I_{\rm sim}(t_i)\propto\int_0^{E_{\rm tot}-D}p(E_{\rm cl})k_{\rm cl}(E_{\rm cl})e^{-k_{\rm cl}(E_{\rm cl})t_i}\,dE_{\rm cl}. \qquad (4)$$

Experimentally, the signal was measured at 25 different delay times t_i ranging from 10 μs to 12 ms. The same set of delays is used to generate the simulated signal for the decay rate fitting procedure. From the calculated time dependence of $I_{\rm sim}$, one clearly sees the effect of the finite width of the energy distribution as a finite offset in the Au_8^+ yield. A similar offset is present in the experimental data (see Fig. 1, middle frame), as summarized in Fig. 3. The simulated data is fitted with the same procedure as the experimental data and the residual decay is quite well approximated by an exponential within the experimental error bars.

The expression for the cluster disintegration rate, $k_{\rm cl}(E_{\rm cl})$, used in Eq. (4), is based on a fit of the experimental data (the left curve in Fig. 2) to the expression

$$\ln(k_{\rm cl})=a_0-a_1/(E_{\rm cl}-D_{\rm cl}). \qquad (5)$$

The values of a_0 and a_1, 12.05 and 1.306 eV, respectively, yield a good fit to the experimental data and include the expected divergence at $E_{\rm cl}=D_{\rm cl}$. The cluster dissociation energy $D_{\rm cl}$ has been measured earlier to 2.65 eV ± 0.09 eV by sequential laser dissociation.[30,13]

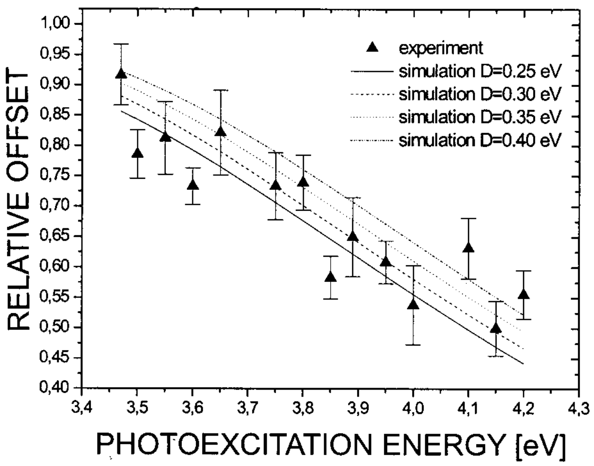

FIG. 3. Experimental and simulated offsets in the decay of Au_8CH_3OH, as described in the text. The offset and the quantum yield are related as yield = 1-offset.

The best simulation of the experimental sequential decay rate constants with the above theory is obtained with the value $D=0.30$ eV. The simulations are shown in Figs. 2 and 3. The three lowest $Au_8^+CH_3OH$ excitation energies are not shown in Fig. 2 since they are out of the range of the measured Au_8^+ rate constants.

The simulation of the rate constants for $D=0.30$ eV is reasonably good but shows a tendency to a smaller slope than the experimental data (see Fig. 2, open circles). This suggests that the energy distribution of the cluster after the methanol has been evaporated may be narrower than calculated.

The fitted experimental offsets for the Au_8^+ yields in the sequential decay data can be compared directly with those from the simulations (Fig. 3). The offset in the long-time abundance of the intermediate cluster, Au_8^+, can only be due to those cluster–molecule complexes that have absorbed a photon and consequently detached the methanol molecule but not yet evaporated a gold atom. It therefore constitutes an absolute experimental measure for which no background subtraction involving photoabsorption cross sections and laser fluences is necessary. Basically the offset is the amount of clusters that contain too little excitation energy to evaporate an atom during the experimental time window. Figure 3 shows the comparison between the experimental offsets and the ones found in the simulations with the values of D given above. The agreement between experiment and simulation is very good, in particular, when one considers that no new fit parameter was introduced in the calculation of the points in this figure.

In addition to the fits of the apparent rate constant and the offset, one more fact is available that can be used to fix the value of D. Upon mass selection, the methanol–cluster compound survives long enough to perform the experiment, i.e., the time until the excitation laser is fired, which is the equilibration time of 150 ms. Therefore, the rate constant is less than about 10 s^{-1} at room temperature. The energy dependence of this rate constant has not been measured and, as mentioned in the Introduction, estimates can be associated with a considerable uncertainty. However, with this caveat we have calculated the rate under the same assumptions about the level densities and the transition state as used in the calculations above. The expression used is Eq. (4) of Ref. 29 with an additional factor for the methanol rotational degrees of freedom. The resulting rate constant at a total energy of $E=0.40$ eV, corresponding to the internal energy of the cluster and the methanol molecule at room temperature, is 60 s^{-1} for $D=0.35$ eV. For a value of $D=0.30$ eV, which fits marginally better in the above figures, the corresponding number would be 2×10^7 s^{-1}, which is in contradiction to the experimental observation, since the methanol–cluster compound would not have survived long enough to perform the experiment. We will therefore favor the value $D=0.35$ eV instead of $D=0.30$ eV, since the discrepancy in the corresponding rates amounts to at least six orders of magnitude.

The best value for D found here, $D=0.35$ eV, differs significantly from an earlier estimate that was based on consideration of the number of IR photons necessary for dissociation and that resulted in the value of 0.6 eV.[10] For comparison, the desorption energy of molecularly adsorbed CH_3OH on a Au(110) surface is 0.52 eV.[31] The estimate was based on a fit of the number of photons absorbed and an RRK calculation that used high-temperature, harmonic oscillator, heat capacities for both methanol and cluster. It is not clear why this procedure would cause a value that is too high, but we consider the value of 0.35 eV more reliable, although systematic errors may still be present.

IV. SUMMARY AND CONCLUSION

Both the measured apparent rate constants and the yields of the second evaporation step in the sequential reaction (1) are reproduced quite well by the adjustment of just one single free fit parameter, which is the cluster–methanol dissociation energy D. The rates in the sequential process are determined by both the average energy of the parent gold cluster and the width of the distribution. The yield contains information on that part of the initial energy distribution that exceeds the energy necessary to induce the sequential reaction (1) within the experimental time window. Both the rates and yields have been simulated, and the comparison between simulation and experimental data shows that the chosen parametrization is reasonable.

The main assumption in the data evaluation is the level density of the gold cluster that determines the partition of energy during evaporation of the methanol from the cluster–molecule compound. Experimental evidence points to a simple transition state that eliminates the need for a detailed and system-specific modeling. The value of the Au_8^+–methanol dissociation energy is found to be $D=0.35$ eV.

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