SUPERSONIC CLUSTER BEAM STUDIES: A STEP TOWARDS MODEL SURFACE INVESTIGATIONS[1)]

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We have observed photodissociation (using visible laser light) of neutral van der Waals clusters (Ar, N_2, O_2, CO_2, SO_2 and NH_3) produced by supersonic expansion and detected by electron ionization/mass spectrometry. Several tests were performed, all of them supporting this surprising discovery. We suggest that Raman induced photodissociation (RIP) is responsible for this phenomenon. The corresponding cross sections are estimated to be in the order of 10^{-23} to 10^{-24} m^2. This first obsservation of Raman photodissociation provides a new technique for the study of neutral van der Waals clusters.

I. INTRODUCTION

Change of physical and chemical properties of matter in the transition to ever smaller units of constituent atoms or molecules is of significant and technological interest. Pherhaps one of the most important changes occurs in the relative contribution of surface constituents to those below the surface (bulk constituents) as a function of cluster size n. Rapid developments in the art of producing and monitoring supersonic cluster beams therefore are beginning to allow a new and alternative approach to surface science, i.e. the study of the interaction of photons and electrons with custom tailored clusters in the high vacuum in much the same way as single crystals have been studied in ultra high vacuum of more conventional surface type experiments. Besides other advantages, in case of cluster studies a much more immediate connection with high level theory is possible.

Here we report as a particularly adapted example of this new approach to surface science recent findings in our laboratory concerning visible laser driven dissociation of gas phase (atomic and molecular) clusters as a function of cluster size (up to $n \sim 150$).

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The *infrared* photodissociation [1] and *ultraviolet* fluorescence predissociation [2] of *neutral*, weakly bound van der Waals clusters, and the *visible* photodissociation of *ionized* clusters [3] have now been studied in a large variety of cluster species. In these experiments a single photon is resonantly absorbed in some well defined vibrational or electronic state above the dissociation limit leading ultimately to the dissociation of the cluster. Conversely, no experiments have been made in the interaction beatween *visible* laser light and *neutral* van der Waals clusters [4] due to the fact that absorbing electronic states in these neutral (e.g. rare gas, molecular) clusters lie energetically beyond the visible range and that therefore no (dissociation) effect could have been expected.

Here, however, we report the results of such a study [5], i.e. the coaxial interaction of visible laser light with neutral Ar, N_2, O_2, CO_2, SO_2 and NH_3 clusters (interaction length 10 cm) produced by supersonic expansion and detected by electron ionization/attachment mass spectrometry [6]. Quite interestingly, this interaction leads to strong photodestruction of the neutral van der Waals clusters, resulting in some cases in the dissociation of more than 80% of certain neutral clusters.

II. EXPERIMENTAL

The supersonic beam/electron impact ionization source/the mass spectrometer system used has been described previously [7]; the only difference is the addition of a Spectra Physics 164 argon ion laser with a nominal power of 5 Watt (all lines). Neutral van der Waals clusters are formed by expanding several bars of the gas studied at various stagnation gas temperatures (between room temperature and liquid nitrogen temperature, respectively) through a 20 μm nozle. The cluster beam thus produced proceeds through a skimmer into a differentially pumped inner chamber. 10 cm down from the nozzle, the cluster beam is crossed perpendicularly by an electron beam. Cluster ions thereby produced are extracted at right angles from the ionization region and analysed in a 90° magnetic sector field followed by a 90° electric sector field. The cluster beam was irradiated co-axially over the entire flight path by a counterpropagating, unfocused cw visible laser beam. In this arrangement, the van der Waals complexes were bathed in the radiation field for a period of appr. 200 μs, corresponding to the flight time from the nozzle to the ionization (detection) region. The laser light was mechanically chopped at 13 Hz; thus photodissociation of the neutral vdW clusters could be detected as a modulation of cluster ion abundances in the mass spectrum. To increase the depletion, we also employed focused laser light in some of the tests. Variation of the irradiation geometry contributed to the confirmation of the nature of the dissociation process.

III. RESULTS

Fig. 1 shows as an illustration in the upper part a conventional Ar_n mass spectrum (obtained without the laser) and in the central part a photofragmentation difference spectrum (up to $n \sim 150$). It can be seen that for all but the smallest clusters, depletion of the original cluster ion signal prevails (negative signal in the difference spectrum) due to strong photografmentation of the neutral precursors. Only for Ar_3^+ and Ar_2^+, a gain due to photofragments from larger clusters (serving as neutral precursors of the respective ion detected) outweighs the loss by photofragmentation of the corresponding original neutral precursors. The turning point between net loss and net gain strongly depends on the stagnation conditions (that is on the neutral cluster distribution) and the ion extraction conditions.

Also shown in Fig. 1 is the fractional change in ion signal induced by the laser beam as a function of cluster size. It can be seen that for small clusters (after the turning point) the fractional loss increases with increasing cluster size, whereas

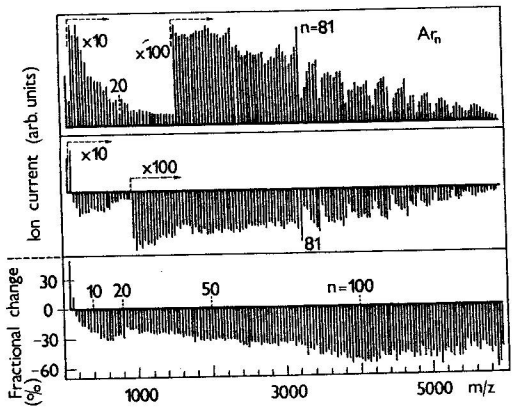

Fig. 1. Mass spectra (computer enhanced display) of an Ar_n cluster beam produced by supersonic expansion (stagnation pressure: 1.5 bar Ar, stagnation temperature: −160 °C, nozzle diameter: 20 μm). The mass spectrum (100 μA electron current, 30 eV electron energy) shown in the upper portion is a conventional Ar_n^+ ($2 \leq n \leq 144$) mass spectrum showing the typical (magic numbers [6]) cluster ion abundances of Ar_n^+ measured without the laser. The mass spectrum below it is a photofragmentation difference spectrum obtained by chopping the laser beam (4.8 Watt laser power) and recording the difference signal between the "laser-on" and "laser-off" time period with a lock-in amplifier. Both spectra are taken under identical expansion and detection conditions. The absolute values cannot be compared directly due to different signal recording devices. The mass spectrum shown in the lower portion gives the fractional change (difference spectrum signal divided by the respective laser-off spectrum signal) in the ion signal in % as a function of cluster size. Some typical identified n values are given above the respective mass peaks.

for large clusters the fractional loss does not depend very much on cluster size, irrespective of the strong dependence of the cluster ion abundance (magic numbers due to special structural features of the respective cluster [6]) on cluster size. Moreover, it should be added that the observed photodestruction of these clusters depends linearly on the laser power (up to appr. 4 Watts). A series of measurements was performed to (i) confirm and prove the existence of this photodissociation process of neutral clusters with visible laser light and (ii) to obtain information about the nature of this dissociation process [5]. For instance, we were able to exclude, by several tests, possible artefacts including photoelectrons from surfaces, the heating of the nozzle and dissociation of the cluster ions present at the crossing point of the electron beam and the cluster beam. Moreover, we extended our studies to N_2, O_2, CO_2, SO_2 and NH_3 clusters [5] and obtained similar photodestruction results as in the case of the Ar clusters.

IV. DISCUSSION

There remains to be discussed the question of the mechanism of this photodissociation of neutral clusters with photons in the visible energy range. As there are no known allowed optical transitions in this wavelength region and taking into account the obsserved characteristics of the dissociation process, the only conceivable inelastic photoncluster interaction depositing energy into the neutral cluster is a spontaneous Stokes-side Raman scattering.

Recently, Godfried and Silvera [8] have observed for the first time rotational and vibrational Raman transitions (Stokes spectra) for the two lowest vibrational states of Ar dimers produced by supersonic expansion. They calculated that some of the $v = 2$ and $v = 3$ states of the Ar dimer are metastable with respect to tunnelling through rotational barriers, the latter state is even strongly predissociating and therefore possibly leading to the observed linewidth broadening in the Raman spectrum. Moreover, Byer and coworkers [9] recently recorded for the first time directly Raman spectra of molecular clusters, i.e. $C_2H_4 \cdot Ar_n$ complexes. These CARS spectra showed at small Ar stagnation pressures a strong signal close to the Q branch of the v_2 vibration of ethylene and at large Ar pressures a red shifted broad peak which is believed to be a shift of the v_2 vibration of C_2H_4 combined with low frequency vibrations of the van der Waals bonds. According to Byer and coworkers one reason for this linewidth broadening could be vibrational predissociation. Moreover, there exist recent observations of first and second order Raman scattering from Ar crystals [10].

In view of these facts and the properties observed at the present time, a Raman excitation of this kind to strongly predissociating states is therefore tentatively suggested as a possible mechanism of the at present obsesrved

photodissociation of Ar, N_2, O_2, CO_2, SO_2 and NH_3 clusters. In contrast to ordinary molecules, where Raman induced excitation cannot lead to dissociation, the extremely weak binding energies of van der Waals molecules (clusters) seem to allow the excitation of predissociating states via the Raman scattering.

Moreover, it is especially interesting to note that various recent studies of atomic and molecular clusters demonstrated that (i) these clusters may be considered above a certain size (appr. 10 to 20) as liquid-like or solid-like structures and that (ii) they exhibit a definite crystal structure (i.e. polyicosahedral) different from possible bulk structures (i.e. fcc). Here we have shown that in the case of VIS photodissociation there exists a smoth transition between the Raman scattering of molecules to Brillouin and/or polariton scattering of crystals. At the present deduced photodissociation cross sections (lying between 10^{-23} to 10^{-24} m^2) are much larger than the normal partial differential Raman cross sections (appr. 10^{-32} m^2 sr^{-1} at 90° detection angle). It is well known, however, that the Raman effect strongly depends on the detection angle and on the excitation energy transferred, and that particular variants of the Raman effect (e.g. surface enhanced Raman scattering) have cross sections of over a millionfold larger then the normal Raman scattering. Moreover, at the present deduced cross section is a *total* cross section including transitions to all of the predissociating states, whereas the *partial differential* Raman cross section mentioned above corresponds only to one specific transition. Finally, taking into account the present results and properties reported for surface enhanced Raman scattering (e.g. see Ref. [10]) we are suggesting tentatively that SERS may be due to a Raman scattering on cluster-like structures present on the surface when several monolayers of adsorbed molecules in SERS studies are used.

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ИССЛЕДОВАНИЯ СВЕРХЗВУКОВЫХ КЛАСТЕРНЫХ ЛУЧЕЙ: ШАГ К МОДЕЛЬНЫМ ПОВЕРХНОСТНЫМ ИССЛЕДОВАНИЯМ

Мы наблюдали фотодиссоциацию (используя видимый свет лазера) нейтральных кластеров Ван дер Ваальса (Ar, N_2, O_2, CO_2, SO_2 и NH_3), возникающих при сверхзвуковом расширении и детектированных посредством электронной ионизации (массовая спектроскопия). Было проведено несколько тестов, причем все подтверждали это неожиданное открытие. Предполагаем, что причиной этого явления является рамановская индуцированная фотодиссоциация. Соответствующие сечения порядка от 10^{-23} до 10^{-24} м^2. Это первое наблюдение рамановской фотодиссоциации открывает новые возможности для изучения неитральных Ван дер Ваальсовских кластеров.