Size-dependent Trends in the Scattering of Small Potassium Clusters by Water Molecules

A. Goldbach[1], F. Hensel[1], and K. Rademann[2]

[1] Fachbereich Physikalische Chemie, Universität Marburg, Hans-Meerwein-Straße,
D-35032 Marburg
[2] Walter-Nernst-Institut, Humboldt-Universität Berlin, Bunsenstraße 1, D-10117 Berlin

Scattering of small potassium clusters by water molecules has been studied in a molecular beam experiment for the first time. In the size range up to eight atoms, trends for cross sections have been obtained by investigating low energy collisions. Significant differences in relative cross sections can be assigned to inelastic collisions. As in case of scattering of sodium clusters by argon (Goerke, A. et al., J. Chem. Phys. **98**, 9653 (1993)), rotational excitation of the clusters seems to be the dominating interaction.

Key words: Potassium clusters, Inelastic scattering, Molecular beam, Mass spectrometry, Photo-ionization.

Introduction

Molecular beam experiments are well established in cluster science, and many investigations on size-dependent properties have been devoted to mesoscopic alkali metal aggregates [1], because they are considered to be prototypes of metal clusters. Furthermore, the electronic structure of these clusters exhibits distinct quantum size effects [1]. While optical and electronic properties have been extensively studied [1], there is relatively little information about the size-dependence of scattering processes involving alkali metal clusters. Actually, besides the mass separation of neutral sodium clusters by size-dependent momentum transfer [2, 3], only scattering cross sections of small neutral sodium clusters have been recently determined for various target molecules [4–7].

Kresin and co-workers [4–6] investigated the small angle scattering of sodium clusters in order to obtain the total cross sections. By passing a collimated cluster beam through a gas cell they measured mass spectra as functions of the scattering gas pressure. For clusters up to 40 atoms, the absolute integral cross sections reached thousands of $Å^2$ with argon, nitrogen, oxygen, various halogen molecules [4], sodium atoms [5], and fullerenes [6] as scattering partners. Assuming an attractive London dispersive interaction, the measured total cross sections were reproduced in a convincing manner by employing experimental polarizabilities and the frequencies of the giant dipole resonance of the clusters [4–6]. In particular, for a given sodium cluster, scattering cross sections grow with increasing polarizability of the different target species [6]. In case of the halogens, the observed cross sections include contributions of reactive scattering, which can be rationalized by assuming an electron transfer mechanism [4], the so-called harpooning model [8].

Goerke et al. studied the interaction of small sodium clusters with neon, argon and nitrogen employing a crossed molecular beam set-up with angular-resolved detection [7]. They investigated the scattering of Na_2 to Na_4 for Ne, and up to Na_8 for Ar and N_2, respectively, and the deflected clusters have been detected within angles of 5° and 55°. In addition, in case of the rare gases classical trajectory calculations were performed using a pure repulsive potential for the description of the cluster-atom interaction. The calculated angular distributions of the scattered clusters matched the experimental data very well in the covered range of detected angles, and the differential cross sections exhibited clear cluster size effects. The calculated absolute integral cross sections are not larger than 200 $Å^2$, however, Goerke et al. pointed out, that in their theoretical approach the long range interactions are underestimated [7]. Both the experimental and theoretical work revealed size-dependent energy transfer to the clusters leading mainly to rotational excitation. Besides that, the experimental data

Reprint requests to Dr. A. Goldbach.

indicated collision induced isomerization of the clusters.

The purpose of the present paper is to contribute to the study of the interaction of alkali metal clusters with water in the gas phase. It is known that Na and Na$_2$ form stable aggregates Na$_{1,2}$(H$_2$O)$_x$ with up to 25 water molecules per cluster, when an effusive sodium beam is exposed to an supersonic beam of a mixture of H$_2$O and Ar [9]. Under these conditions sodium atoms are expected to undergo many collisions with water molecules [9]. In contrast, we report for the first time on the interaction of small potassium clusters with water molecules under single collision conditions.

Experimental

We have passed a potassium cluster beam through a scattering cell containing water gas, and in order to cover a broad range of scattering angles, the cell has been positioned right in front of the entrance of a reflectron time of flight mass spectrometer. The molecular beam apparatus is schematically shown in Figure 1. It is composed of the cluster beam source (O) in a first vacuum chamber (VC I), the gas scattering cell (SC) and the mass spectrometer (MS). The latter devices (SC, MS) are placed in a second vacuum chamber (VC II) [10]. Radiation of a pulsed N$_2$-laser (L) with an energy of 3.67 eV has been employed for

photoionization of the neutral clusters. With the exception of K and K$_2$, a single photon of this energy suffices for ionization of potassium clusters [11]. Ion detection has been accomplished by a Daly-type scintillation detector (DT) [12]. Both vacuum chambers are pumped by unbaffled oil diffusion pumps which are backed by a combination of a roots blower and a rotary pump. During the expansion the pressure rises to 10^{-3} mbar in the first chamber and reaches a maximum of $3 \cdot 10^{-5}$ mbar in the second chamber.

Emphasis has been put on establishing an alkali metal cluster beam with long-term stability. For that reason, a new type of high temperature metal vapour oven (Fig. 2) has been developed to produce clusters by seeded supersonic expansion. It is built of stainless steel and consists of a reservoir (A) and an expansion chamber (D), which are both equipped with separated independently controlled electric resistance furnaces made of molybdenum wire. These two parts of the cluster source are connected by a small tube which allows the separate regulation of the temperatures of both components. So, the potassium vapour pressure and the expansion temperature of the gas mixture can be adjusted independently.

Temperatures are controlled by chromel-alumel-thermocouples, which are placed in an appropriate cavity (G) in the expansion chamber and in a small tube (B) inserted in the reservoir vessel. Differences up to 200 °C can be maintained between the expansion chamber and the reservoir, while at the same time
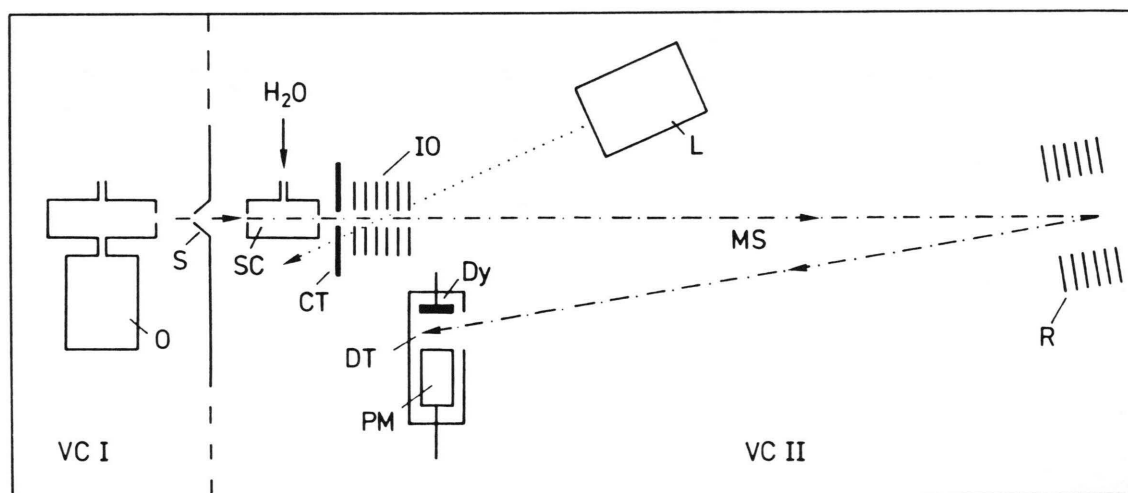

Fig. 1. Experimental set-up: (VC I) first vacuum chamber, (VC II) second vacuum chamber, (O) oven source, (S) skimmer, (SC) scattering cell, (CT) shield attached to N$_2$ (l) cooling trap, (MS) mass spectrometer, (IO) acceleration ion optics, (R) electrostatic reflector, (DT) Daly detector with (DY) dynode and (PM) photomultiplier, (L) N$_2$-laser.
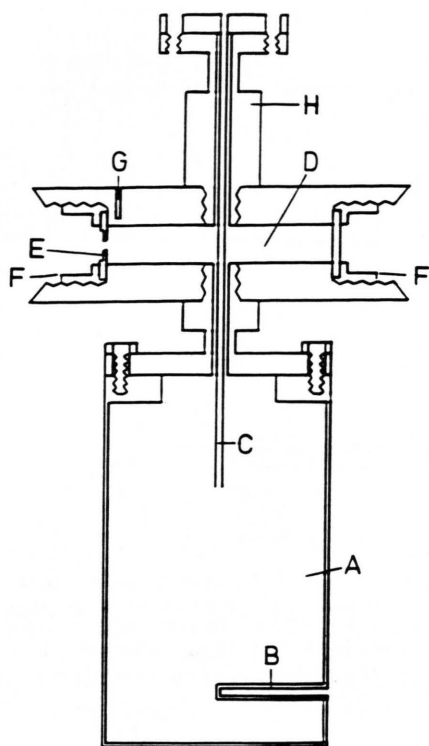
Fig. 2. Cluster beam source: (A) reservoir vessel, (B) capillary tube for thermocouple, (C) seed gas inlet, (D) expansion chamber, (E) nozzle plate, (F) Allen screws, (G) opening for thermocouple, (H) connection to mounting flange.

temperatures do not vary from the average by more than 2 °C. In particular, the expansion chamber has to be kept at least 40 °C above the reservoir temperature to prevent the nozzle from clogging. Nozzle plates (E) are made of stainless steel. They are screwed into the body of the expansion chamber with Allen screws (F). Nozzle openings are cylindrical, measuring 0.2 mm in diameter. The length of the nozzle channel can be varied from 0.5 to 2 mm. Graphite foil serves as sealing material for all contacting interfaces of the oven components. The Allen screw threads are greased with a paste containing copper and molybdenum disulphide to reduce corrosive jamming at elevated temperatures. A capillary tube (C) introduces the argon into the reservoir, where it mixes thoroughly with the metal vapour. Argon is added to raise the stagnation pressure in the oven. The reservoir is kept at temperatures between 600 °C and 700 °C, corresponding to potassium vapour pressures of 150 mbar and 500 mbar, respectively. The stagnation

pressure is varied from 600 mbar to 1000 mbar. In this way, molecular beams have been obtained with constant cluster distribution for more than 10 hours.

The oven source (O) is mounted on a flange, which hangs in the first vacuum chamber. The connection (H) between the oven and the mounting flange is also equipped with a molybdenum resistance heater. The molecular beam is horizontally aligned by rotation of the flange and vertically by altering the tension of a preloaded disk spring assembly. The distance between the nozzle and a heatable skimmer (S) is 45 mm. The skimmer separates the oven vacuum chamber from the second one, where the cluster beam passes through the gas scattering cell (SC). The circular entrances of the cell are 0.5 mm in diameter and the scattering zone is 80 mm wide. The distance between skimmer and scattering cell is 20 mm. The cell is connected with a water vapour reservoir, i.e. a vessel, that is half-filled with liquid water at room temperature. A needle valve regulates the water gas flow into the scattering cell. The pressure in the cell has not been measured directly, but the scattering gas density N_z has been related to the adjustment of the needle valve, what will be explained in the following section. The gas cell is positioned in front of the electrostatic ion acceleration optics (IO) of the mass spectrometer at a distance of 45 mm. The total distance between the oven nozzle and the ionization region is 200 mm. A shield (CT) fixed to a cryo trap surrounds the ion acceleration assembly and protects it from residual water and metal vapour. The cluster beam and the laser radiation pass the shield through convenient openings. The reflectron mass spectrometer is aligned with the cluster beam. The ionized particles are reflected at a distance of 800 mm (R) and arrive at the Daly-detector (DT) after another 600 mm drift length. The angle of reflection is 3° and resolution of the mass spectrometer is 250 amu.

Figure 3 presents the layout of the acquisition electronics. Mass spectra are recorded with a LeCroy 9400 oscilloscope. After conversion by a level adapter
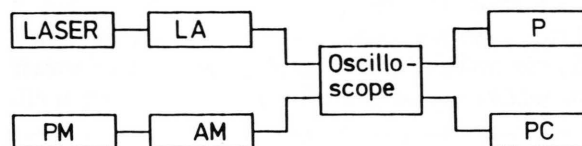

Fig. 3. Layout of acquisition electronics: (PM) photomultiplier, (PC) personal computer, (LA) leveladapter, (AM) amplifier, (P) plotter.

(LA) unit, a voltage pulse from the laser triggers the oscilloscope. In the scintillation detector the photomultiplier (PM) produces a photo current corresponding to the transient ion current. This signal is amplified (AM) and displayed on the screen of the oscilloscope. A reasonable number of these spectra is added up to remove statistical fluctuations. The averaged mass spectra are stored on a personal computer (PC) or, alternatively, printed out on paper (P).

Results and Discussion

We obtained mass spectra of neutral potassium clusters that show the usually observed intensity modulations [1], i.e. the cluster intensities in the beam drop rapidly after those with 8, 20 and 40 atoms. These modulations reflect the electronic shell structure of the clusters [13, 14]. In the present work we concentrate on the scattering of aggregates up to K_8. Figure 4 shows typical mass spectra of this size range employing nozzles of different geometry: varying the length of the nozzle channel from 0.5 to 2 mm alters the cluster distribution significantly. This effect indicates insufficient cooling of the clusters by the supersonic expansion so that additional cooling occurs by the evaporization of atoms. Lengthening of the nozzle channel facilitates the cooling by the expansion, for K_8 increases and K_7 decreases in the cluster distribution, for instance.

Apart from the pure metal clusters some mixed potassium oxygen aggregates (e.g. K_3O, K_4O and K_5O_2) can be identified in the mass spectra (Figure 4). Formation of oxidized species [10] is due to an oxygen impurity in the argon of about $2 \cdot 10^{-3}\%$, but this will be described in detail elsewhere [15]. In order to suppress the oxidized clusters, the fraction of argon has been reduced in the oven source, though this decreases the cooling in the supersonic expansion. Therefore in the present work the primary cluster distribution is established by evaporative cooling.

In order to determine the scattering cross sections, we compare the cluster intensities of beams passing through the scattering cell, with and without water vapour inside. Figure 5 displays the relative cluster abundance in mass spectra which are recorded at different scattering gas densities. In this figure each cluster intensity I is normalized to the cluster intensity I_0 of the primary beam, that is obtained without water in the cell. The water gas density has been increased
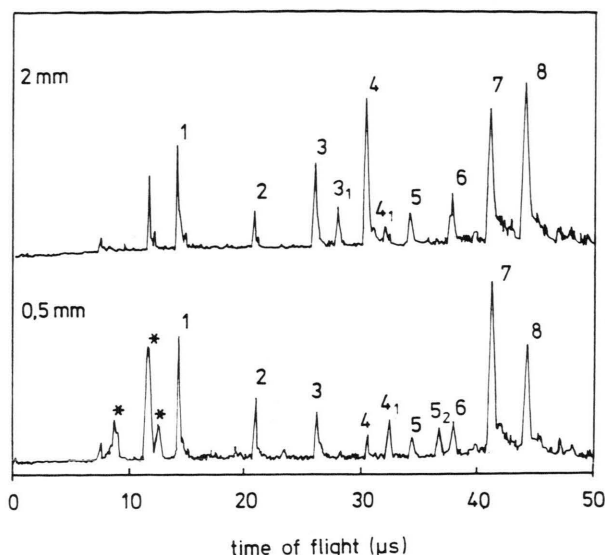

Fig. 4. Typical mass spectra of the primary cluster beam obtained at 3.67 eV in the size range up to K_8, employing cylindrical nozzles of 0.5 and 2 mm channel length. Longer channels lead to increased cooling. The numbers with subscripts denote oxidized clusters (e.g. $5_2 = K_5O_2$). The asterisks denote H_2O, N_2 or O_2.
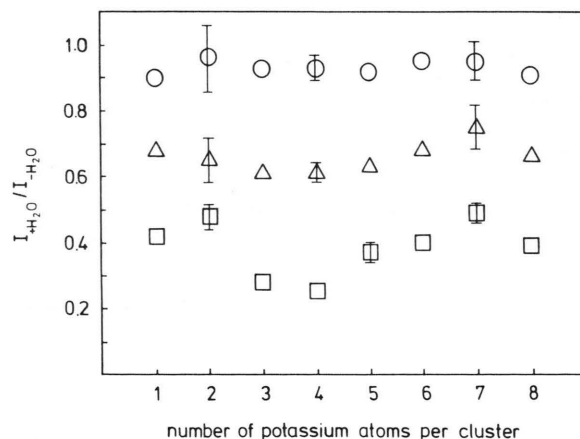

Fig. 5. Cluster intensity I in the presence of water in the scattering cell, normalized to the intensities I_0 obtained without scattering gas. The mass spectra are taken at different N_Z, denoted by overall decreases of 5% (circles), 35% (triangles) and 65% (squares).

gradually, leading to counting rate decreases of up to 70%. The average center of mass collision energies vary from 0.08 eV for K to 0.11 eV for K_8. Obviously the deflection of the clusters is size-dependent.

The measurements have been carried out under single collision conditions. For K_7 and K_8 this is demon-
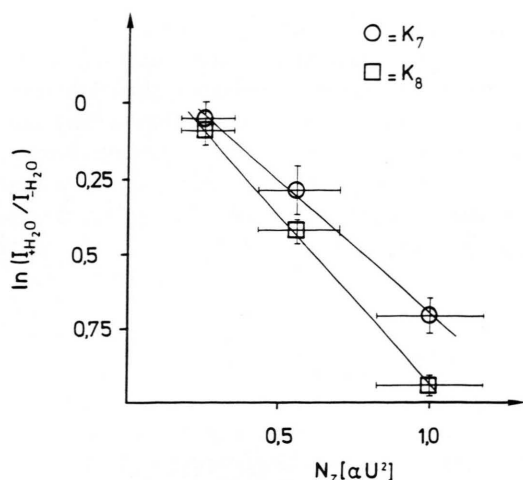
Fig. 6. Logarithm of the relative cluster intensity (I/I_0) as function of scattering gas density N_Z, which is denoted by the square of the arbitrary unit U (as described in the text), for clusters K_7 (circles) and K_8 (squares).

strated in Fig. 6, which displays the logarithms of the relative cluster intensities (I/I_0) plotted versus the water gas density N_Z in the scattering cell. Although the pressure has not been gauged directly, N_Z has been estimated in the following reproducible way [10]: the reservoir vessel contains water vapour in equilibrium with the liquid phase at room temperature. Therefore a stationary water gas density is obtained in the scattering cell for each adjustment of the needle valve. From considerations made upon the mechanism of the valve, it follows that the density N_Z increases quadratically with the turning of the needle in the valve [10]. This motion is scaled in arbitrary units of U. Hence, N_Z is scaled in U^2 in Figure 6. The straight lines of this plots are in agreement with Beer's law

$$I = I_0 \exp(N_Z l \sigma), \qquad (1)$$

where l is the scattering cell length and σ the scattering cross section. (The plots do not intercept the intensity axis at zero because the assumption of a linear interdependence between N_Z and U^2 does not hold any longer when the needle valve is virtually completely closed.) The corresponding plots of the clusters K to K_6 show also linear slopes. It is clear from (1) that these slopes are proportional to the scattering cross sections σ. Thus we are able to determine relative cross sections σ^{rel} in the size range up to K_8 (Table 1). However, it must be pointed out that the counting rates of K and K_2 have to be analyzed with caution

because the ionization of these species requires two photons of 3.67 eV. Fluctuations of the laser radiation do not change the relative cluster abundance of K_3 to K_8, but the relative intensities of K and K_2 are seriously affected. For that reason in the following considerations K and K_2 are left out.

For the interpretation of our scattering results we refer to the above mentioned work on scattering of sodium clusters. In general, our data are more instructive to be compared with the results of Goerke et al. [7] than those of Kresin and co-workers [4–6]. Mere long range interactions of the van der Waals type produce only weak deviations of the clusters from the beam axis. Because of the design of our experiment, a quite strong deflection of the clusters is required to prevent them from entering the ionization region. Accordingly, the long range interactions can not contribute essentially to the scattering behaviour of potassium clusters observed in the present investigation. So, we compare the scattering of potassium clusters by water molecules with the scattering of sodium clusters by argon atoms as studied by Goerke and co-workers, which reflects more the situation at close encounter of the interacting particles [7].

In Figure 7 relative cross sections of this work and the calculated values of Goerke et al. are displayed.

Table 1. Relative cross sections σ^{rel} for scattering of K_x by H_2O derived from slopes of plots due to Beer's law (see text).

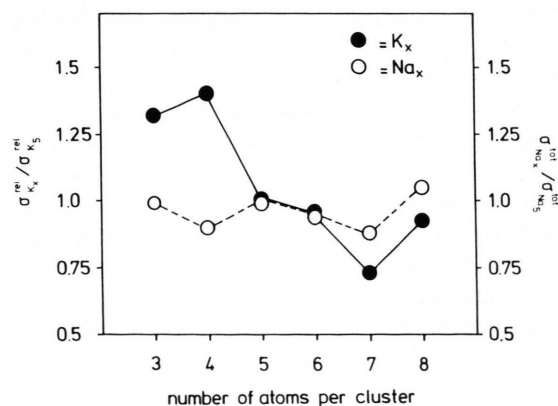| x	1	2	3	4	5	6	7	8
σ^{rel}	1.02	0.92	1.60	1.70	1.21	1.15	0.88	1.13

Fig. 7. Relative cross sections for scattering of K_x by H_2O (this work) and Na_x by Ar (derived from [6]) in the range from $x = 3$ to $x = 8$.

Concerning the sodium clusters, the absolute integral inelastic scattering cross sections σ^{tot} have been divided by the cross section of Na_5 in order to obtain relative values. As well, the relative cross sections σ^{rel} of the present investigation (Table 1) have been divided by that of K_5. Especially for clusters with 5 and more atoms, the overall trend for potassium clusters goes together with that of sodium clusters, and in both investigations the cluster with 7 atoms is least affected by the respective scattering gas. Part of the deviations are due to neglecting the effect of the finite angular resolution of the experimental set-up on the potassium cluster results. Only those potassium clusters are not detected after the scattering event, which are deflected by more than a certain limiting value. Hence the derived relative cross sections are too small, and the error increases systematically with cluster size, because the heavier the cluster the less it will be deflected in a collision. This has the following effect on Figure 7. The relative cross sections for potassium clusters smaller than K_5 are overestimated in this type of presentation, whereas the values belonging to the heavier aggregates are too small. Taking this into account, the consistency between both investigations on the scattering of alkali metal clusters becomes even more evident.

Under the conditions employed by Goerke et al., the collisions of small sodium clusters with argon are dominated by inelastic processes, leading mainly to rotational excitation of the clusters [7]. Therefore we believe that this interaction mechanism also accounts for scattering of small potassium clusters by water molecules as reported here. The efficiency of rotational energy transfer is governed by the magnitude of the moment of inertia of the clusters. Concerning the alkali metals potassium and sodium, the calculated ground state structures [16–21] of M_3, M_4 and M_5 (M = Na, K) are planar. Whereas M_6 is a pentagonal pyramide and Na_7 a pentagonal bipyramide, the most stable isomer of Na_8 is a dodecahedron. To our knowledge, no calculations have been performed on the ground state structures for potassium clusters with more than 6 atoms. However, for clusters up to K_6 the ground state geometries correspond with those of the sodium clusters [16]. Therefore we adopt the same geometries for K_7 and K_8 as those which have been calculated in case of Na_7 and Na_8.

Among these clusters, M_3 and M_7, have the most compact structures [17]. Accordingly, M_3 and M_7 owe the smallest moments of inertia, and rotational excita-

tion requires the greatest energy transfer in the collisions. This corresponds with the experimental observation that K_7 is the least deflected cluster in our investigation. Similarly, Na_7 exhibits the smallest calculated cross section for scattering by Ar, although it has been pointed out that the experimental cross section disagrees with the calculated value in that special case [7]. This is due to the fact that Na_7 is the only cluster in this size range which has a high probability to take an energetically less favoured configuration [17]. For example, at 100 K 80% of the Na_7 clusters occupy configurations that are much more extended than the ground state structure which has been used for the calculations [7]. Rotational excitation of the extended configurations is much more probable. Concerning the present work, this implies that the K_7 clusters, and the other K_x clusters as well, are cold enough to take the ground state configuration.

The scattering behaviour of clusters M_3, however, disagrees with this picture, and in the present investigation the relative cross section obtained for K_4 seems to be exceptionally large. This is indicative of other interaction mechanisms. Actually, Goerke and co-workers found that in case of Na_3 also significant vibrational excitation resulted after the scattering event with argon [7]. In addition, they have evidence for isomerization of the clusters Na_3 and Na_5 after the collision. These inelastic interactions may also occur in the collisions of small potassium clusters with H_2O, but reactive scattering of K_x has to be taken into consideration as well. Moreover, the complete neglection of induced dipole/induced dipole (London dispersive) and dipole/induced dipole interactions may be inappropriate concerning this investigation. Finally, it must be kept in mind that in the case of the scattering partner H_2O rotational and vibrational energy levels are accessible.

Summary

We have observed low-energy scattering of potassium clusters by water molecules in a molecular beam experiment under single collision conditions. For clusters with up to eight atoms, trends are reported. From qualitative agreement with calculations on the scattering of small sodium clusters by argon [7] we conclude that inelastic processes dominate the scattering in our investigation. Energy transfer due to rotational excitation is consistent with our experimental data. More

refined measurements are desirable, not only because of the lack of quantitative data but also in order to decide upon further scattering interactions.

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