Nondestructive Mass Selection of Small van der Waals Clusters

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Clusters of atoms or molecules have been extensively studied by a variety of spectroscopies because of their unusual properties. Experiments with van der Waals clusters of defined sizes are not easily possible because nozzle beam expansions used in their production yield broad size distributions. Moreover, being weakly bound they readily fragment in the commonly used electron impact–ionization mass spectrometer detectors. Here it is shown that light fragile clusters of He, H₂, and D₂ can be selected and identified nondestructively by diffraction from a transmission grating. The method is universally applicable also to heavier species and well suited for spectroscopic studies.

 ${f T}$ he experimental and theoretical study of clusters of atoms and molecules has become an important emerging area of chemical physics. Intermediate in size between individual atoms and molecules and bulk matter, clusters provide insight into how the properties of bulk matter evolve from those of their atomic constituents (1). In nozzle beam expansions, a large variety of small, weakly bound clusters of different composition can be formed. From their spectroscopic investigation, which is being actively pursued in many laboratories, one hopes to gain insight into the extent to which, for example, pairwise additive forces can explain the intramolecular interactions and when nonpairwise forces come into play. At present, it is usually not possible either to select or to detect and identify quantitatively small van der Waals clusters. Detection by mass spectrometry suffers from the indistinguishability of the signals at small masses and of those signals resulting from the fragmentation of larger clusters (2). Moreover, small clusters dissociatively ionize to an unknown extent and for very weakly bound species may dissociate almost entirely so that they become difficult to detect. For selecting and characterizing clusters of different sizes, several different deflection scattering techniques have been developed, but these are restricted either to large clusters $(N \ge 500)$ (3–6) or to small, tightly bound clusters ($N \leq 10$) (7, 8).

To circumvent these problems, we developed a technique in which molecular beams containing clusters produced in a conventional nozzle beam expansion are diffracted from a transmission grating. The use of similar gratings for diffracting atomic beams has been demonstrated recently (9, 10), but the resolution in these pioneering experiments was much less than that reported here. The cluster size selectivity in

our experiment derives from the narrow velocity (v) distribution in nozzle beam expansions, typically $\Delta v/v \lesssim 5\%$ so that all clusters of different sizes have nearly the same velocities. Thus, the de Broglie wavelengths (λ) of the clusters will be inversely proportional to the number of atoms (N) in the clusters such that

$$\lambda = \frac{h}{N \cdot m \cdot v} \tag{1}$$

where h is Planck's constant and m is the mass of the cluster constituents. In the Fraunhofer approximation, the diffraction angles for a beam normally incident on a grating are given by

$$\sin \theta = n \frac{\lambda}{d} = n \frac{h}{N \cdot m \cdot v \cdot d}$$
(2)

where n is the diffraction order and d is the grating period. In the experiments described here, we consider mostly low-order diffrac-

tion (n = 1, 2, 3), with small diffraction angles ($\sim 1 \text{ mrad}$) so that Eq. 2 simplifies to $\theta \propto N^{-1}$. This technique is entirely nondestructive because only those particles that pass the grating can contribute coherently to the diffraction peak intensity.

Diffraction of He Clusters

The beams in Fig. 1 were produced by expanding the gas through a 5-µm-diameter orifice from a source chamber, which can be cooled from 300 K down to 5 K. To achieve sufficient spatial coherence, we collimated the beam by two slits (10 μ m by 3 mm) located 47 cm apart. An additional chamber can be placed in the beam between the slits for scattering experiments. The silicon nitride grating has a period of 200 nm, with bars and slits of 100 nm width, an overall height of 1 mm, and an overall transmission of about 35%, which is less than 50% because of support struts (11). The diffracted beams were detected by a homemade mass spectrometer, which is located in a separate vacuum chamber with a base pressure of 7 $\times \ 10^{-11}$ mbar and can be precisely rotated through small angles around an axis parallel to the slits and centered at the grating. A 25- μ m slit at 53 cm from the grating serves to collimate the beam before it enters the detector. The ionizer is typically operated at an electron energy of 60 eV and a current of 9 mA and has a sensitivity for He atoms of about 10^{-6} per incident atom.

The diffraction patterns can be detected by the mass spectrometer operating in two different modes. Typically, the direct inflight ionization mode is used. Here, the mass of any fragment ion can be chosen because the diffraction angle identifies the



Fig. 1. Schematic diagram of the apparatus used for diffraction of the different components in a He cluster beam. Only the vacuum system containing the ionizer is indicated. BF designates the beam flag that intercepts the incident beam in the stagnation mode measurements. The inset (bottom right) shows a scanning electron microscope picture of the grating used (*10, 11*).

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clusters. For example, in the case of H_2 , where the background on the constituent mass H_2^+ is notoriously large, another ion mass that is not present in the background (such as H_3^+) can be chosen. In the stagnation mode, we first destroyed all the clusters by allowing them to strike a flag (Fig. 1) placed in front of the ionizer. The resulting pressure buildup in the ionizer vacuum chamber is then detected by the mass spectrometer. This signal is proportional to the flux of constituent atoms or molecules transported into the detector chamber, and if one knows the size of the clusters, the average flux of clusters can be ascertained. In the case of He cluster beams, the ionizer can be simply calibrated as with conventional leak detectors.

Most of our initial experiments were carried out with He clusters because of the great current experimental (12) and theoretical (13) interest in the He dimer. Figure 2 shows two angular distributions measured for He expanded from a source temperature (T_0) of 300 K and source pressure (P_0) of 150 bar and from $T_0 = 150$ K and $P_0 = 170$ bar. Even at 300 K, where the He atom de Broglie wavelength is 0.56 Å, diffraction peaks out to the 11th order can be detected; the signal in the first-order peak is 10⁴ counts per second and the background is less than 10^2 counts per second. The alternation of intensities favoring the odd-order peaks is expected for a grating with bars and slits of equal width. At 150 K, the de Broglie wavelength is 0.78 Å and the dispersion is increased and new structures appear that are especially apparent halfway between the central zero order and the first-order He atom diffraction peaks. From the diffraction angles, we assign these new structures to He dimers. Previously, only dimers of Na could be detected by a similar technique (14).

For a closer look, we reduced T_0 to 30 K ($P_0 = 15$ bar) where $\lambda \approx 1.81$ Å. Figure 3 shows angular distributions measured in three different ways: in the direct ionization mode with the mass spectrometer set at mass (m) = 4 atomic mass units (amu) (He⁺) and with m = 8 amu (He₂⁺). Only the distribution of signals between the central n = 0and n = +1 He atom peak is shown. The two additional peaks seen in Fig. 3, A and B, appear at diffraction angles, indicating that they are a result of the He dimer and trimer (15). The results of angular distributions measured in the stagnation mode (Fig. 3C) confirm these results. These experiments provide direct unequivocal evidence for the existence of the He dimer and trimer. Mass spectrometer evidence for the dimer has been recently reported (12), but its existence is still the subject of considerable controversy (16, 17). The He dimer is a particularly interesting molecule, predicted to have a weak binding energy of only 1.3 imes

heavier rare gases—that is, for Ar the same ratio is 0.6 (7). By comparing the sum of the signals in Fig. 3, A and B, with the number flux evaluated from Fig. 3C, we determined

the ratio of the ionization cross sections for

He₂ and He₃ with respect to the cross sec-

tion for ionization of the atoms. The results

are 2.45 and 3.2, respectively, which is within probable errors equal to the values

2.0 and 3.0 that are expected if the ioniza-

tion cross section depends only on the num-

 10^{-3} K. With an average internuclear dis-

tance of about 50 Å (13), it is considered to

Implications

These and other results contain much in-

formation on the various properties of He

dimers and trimers, their ionization behav-

ior, and their creation in nozzle beam ex-

pansions. For example, we measured the

total integral scattering cross sections for all

of these species (18). From comparisons of

the angular distributions in Fig. 3, A and B,

the ratio of electron impact fragmentation

of He₂ to form He₂⁺ relative to He⁺ is

conservatively estimated to be less than

0.10 and is significantly smaller than for the

be the world's largest diatomic molecule.

ber of atoms in the cluster, as expected for such weakly bound clusters. At a somewhat higher source pressure than that shown in Fig. 3 ($P_0 = 20$ bar), the He⁺ signal from He₃ reaches a maximum



Fig. 2. Two angular distributions for He cluster beams, measured at $T_0 = 300$ K and $P_0 = 150$ bar (**A**) and at $T_0 = 150$ K and $P_0 = 170$ bar (**B**). Note that the logarithm of the He⁺ signal measured in the direct in-flight mode is plotted versus the deflection angle. The numbers indicate the diffraction orders of the He atom diffraction peaks. The asterisks in (B) denote additional peaks attributable to first-order diffraction of He dimers.

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where it is more than 4.5 times greater than the He⁺ signal from the He₂ and He₄ clusters. This large enhancement is of considerable interest in connection with the question of the existence of Efimov states. In 1970, Efimov (19) first predicted that three bosons will have an infinite number of special long-range bound states, which are now called Efimov states, in the limit that the two-body interaction approaches zero binding energy. So far, Efimov states have not been found in nuclear systems, but there is now some evidence that they may exist for He₃ because of the very weak binding energy of He_2 (20). At high source pressures of $P_0 = 60$ bar, it was not possible to resolve any of the small clusters although the conditions are expected to strongly favor cluster production. The slight broadening of the central peak suggests that under these conditions only very large clusters are produced. Moreover, pressure-dependent studies suggest that the trimer and possibly the tetramer are the critical clusters as invoked in the classical Gibbs (1876), Vollmer-We-



Fig. 3. Angular distributions measured in three different ways are shown for a He cluster beam produced at $T_0 = 30$ K ($P_0 = 15$ bar). In (**A**) and (**B**), the cluster beam components are ionized directly in-flight. In (**C**), the beam flag (BF in Fig. 1) intercepts the primary beam, and the stagnation pressure increase in the detector chamber is measured. The mass spectrometer records the signals at 4 amu (He⁺) in (A) and (C) and at 8 amu (He_p⁺) in (B). Note scale factor in (A) and (C).

ber (1925), and Becker-Döring (1935) theories of cluster condensation (21), which are still in use. Previously, information on these critical clusters could be obtained only indirectly (22).

Results for D₂ and H₂

Figure 4 shows similar measurements for a cryogenic beam of D_2 produced at $T_0 = 50$ K and $P_0 = 40$ bar. Again, only the region near the first-order diffraction peak is shown. The overall resolution is not as good as with He, because in these earlier experiments wider slits were used. Angular scans measured in the direct in-flight detection mode for masses of 4 amu (D_2^{+}) and for 6 amu (D_3^+) [which can result only from the ionization of $(D_2)_N$ show significant differences. The D_2^+ scan shows an intense, first-order diffraction peak, indicating a large D₂ monomer signal. The broad central peak is an indication of larger unresolved clusters. The D_3^+ scan shows two peaks attributable to first- and third-order diffraction of the D₂ dimer at θ = 0.45 and θ = 1.35 mrad, respectively. The shoulder at θ = 0.25 mrad corresponds to the location of the D_2 trimer. Surprisingly, the D_3^+ central peak is narrower than that measured with D_2^+ . Apparently, the large clusters do not



Fig. 4. Two angular distributions for a D₂ cluster beam produced at $T_0 = 50$ K and $P_0 = 40$ bar. In the top panel, the clusters are ionized directly inflight and the ion signal on m = 4 amu (D₂⁺) is measured. A well-resolved peak is seen only for first-order diffraction of the uncondensed D₂ molecules. In the bottom panel, the ion signal on m =6 amu (D₃⁺) shows peaks for (D₂)₂ dimers for n =1 and 3. Also at $\theta = 0.25$ mrad, a shoulder that is attributed to (D₂)₃ (n = 1) is apparent.

fragment to D_3^+ but to larger cluster ions. Figure 5 shows similar measurements for H_2 clusters; here, the large detector background on masses of 1 amu (H^+) and 2 amu (H_2^+) was circumvented by setting the mass spectrometer to a value of m = 3 amu (H_3^+). Thus, only cluster ion fragments can be detected and the H_2 dimer and H_3 trimer are clearly resolved. There are also weak peaks only slightly above the noise level corresponding to N = 4, 6, and 8.

Conclusions

As illustrated by the results presented here, this diffraction technique is especially suited for the study of He cluster beams, because of their large de Broglie wavelength at the low source temperature, the inherent low detector background on the He mass, and the narrow velocity distributions of He nozzle beams. For He cluster beams with relative velocity half-widths of $\Delta v/v =$ 3.3%, our calculations reveal that this resolution is not limited by the velocity spread nor by the number of grating slits illuminated but only by the divergence of the beam-that is, by the spatial coherence of the wave packet. Thus, the size of the largest cluster ($N_{\rm max}$) that can be resolved for a given angular resolution (taken from the angular width of the central peak) can be simply derived from Eq. 2 as follows:

$$N_{\rm max} \simeq 2 \left[\frac{nh}{\sqrt{5m \, kT_0 \, d \, \Delta\theta}} \right]^{1/2} \qquad (3)$$

where we have used the expression $v = \sqrt{5 \cdot m^{-1} kT_0}$ for fully expanded nozzle beams (23). Thus, the constituent mass *m* and source temperature T_0 do not enter into the equation as strongly as the grating period *d* and $\Delta \theta$, the product of which defines



Fig. 5. An angular distribution for an H₂ cluster beam produced at $T_0 = 40$ K and $P_0 = 10$ bar and detected in the direct in-flight mode. The mass spectrometer is set at m = 3 amu (H₃⁺). The expected first-order diffraction peak locations are indicated for (H₂)₂, (H₂)₃, (H₂)₄, (H₂)₆, and (H₂)₈.

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the figure of merit of the device. In this apparatus, $\Delta \theta$ is determined by the geometry of the 10- μ m slits to be $\Delta \theta = 70 \mu$ rad. In the course of our experiments here, the best mass resolution in the first order (n =1) was achieved for ⁴He at T = 15 K and corresponds to roughly $N_{\text{max}} = 8$, which means that He_8 could be distinguished. By reducing the slit width by a factor of 2, reducing the source temperature to $T_0 =$ 7.5 K, and using a grating with d = 100 nm, we can easily increase the resolution to $N_{\text{max}} = 20$, making it possible to separate ${}^{4}\text{He}_{21}$ from ${}^{4}\text{He}_{20}$. The same apparatus is also very well suited to investigate clusters of the fermions ³He. Recent theories Iwhich include the effects of Fermi statistics of the very cold clusters (T < 0.4 K)] indicate a sequence of stable clusters (magic numbers) resulting from the closing of shells (24) as in the electronic shell structure of atoms. With ³He clusters, it should be possible to observe clusters up to $N \cong 30$, which is well within the range of clusters where such effects should be observed. In the case of molecules, the symmetry of the electronic wave functions also affects the symmetry of the rotational states (j). The effect of symmetry on the stability of clusters can be explored by comparing para-H₂ (j = 0, 2, ...) or or-tho-D₂ clusters (j = 0, 2, ...) with normal H₂ clusters [25% para-H₂ and 75% ortho- H_2 (j = 1, 3, ...)] and normal D_2 clusters $[33\% \text{ para-D}_2 (j = 1, 3, ...) \text{ and } 67\%$ ortho-D₂], respectively. With this technique it should also be possible to carry out high-resolution spectroscopy on sizeselected clusters (25). Radiation can be directed at the beam before or after passage through the grating, and the resulting depletion of the signal because of the destruction of a given size cluster can then be observed.

In summary, we have demonstrated the utility of transmission diffraction gratings for the nondestructive mass selection and identification of small van der Waals clusters. With the use of a mass spectrometer as a detector, the various ion fragmentation channels of the clusters can be explored. Currently, gratings of 100 nm are available (26) and gratings of 50 nm are possible (27). We estimate that with a 50-nm grating (provided the relative velocity spread after velocity selection is less than 3%), it should be possible with our apparatus to separate trimers of species with de Broglie wavelengths of $\lambda \ge 0.10$ Å, such as for a beam of Xe at $T_0 = 300$ K.

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Calcium-Calmodulin Modulation of the Olfactory Cyclic Nucleotide-Gated Cation Channel

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Although several ion channels have been reported to be directly modulated by calciumcalmodulin, they have not been conclusively shown to bind calmodulin, nor are the modulatory mechanisms understood. Study of the olfactory cyclic nucleotide-activated cation channel, which is modulated by calcium-calmodulin, indicates that calcium-calmodulin directly binds to a specific domain on the amino terminus of the channel. This binding reduces the effective affinity of the channel for cyclic nucleotides, apparently by acting on channel gating, which is tightly coupled to ligand binding. The data reveal a control mechanism that resembles those underlying the regulation of enzymes by calmodulin. The results also point to the amino-terminal part of the olfactory channel as an element for gating, which may have general significance in the operation of ion channels with similar overall structures.

I on channels are subject to modulation that enhances their functional flexibility by various noncovalent or covalent structural modifications, the most common being phosphorylation by protein kinases (1). These modifications can alter voltage- or ligand-sensitivity, probability of opening,

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other properties (1). Among ion channel modulations, one unusual form involves an apparently direct interaction between calcium-calmodulin (Ca²⁺-CaM) and the channel protein. Channels showing this property include Ca2+-dependent sodium and potassium channels in Paramecium (2), the ryanodine receptor channel in muscle (3), and a K^+ channel in kidney (4). More recently, the cyclic nucleotide-activated cation channels mediating visual and olfactory transductions have also been found to be apparently modulated directly by Ca2+-CaM (5, 6). The modulation of the olfactory channel is particularly pronounced, with the apparent affinity of the channel for cyclic nucleotide reduced by more than an

rate of desensitization or inactivation, or

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order of magnitude in the presence of Ca²⁺-CaM (6), a property probably important for olfactory adaptation (7, 8). The retinal and olfactory channels share features with voltage-activated, Shaker-type K⁺ channels, including six putative transmembrane domains (one being an S4-like domain), cytoplasmic amino and carboxyl termini, and a conserved pore-forming region (9-11). One distinctive feature of the retinal and olfactory channels, however, is a cyclic nucleotide-binding site in the COOH-terminal segment which, when bound to ligand, leads to activation of the channel (9, 10). Both the native rod and olfactory channels are composed of α and β subunits (also called subunits 1 and 2) that have 30 to 50 percent amino acid identity and a similar hydropathy pattern, even though only the α subunit can form functional cyclic nucleotide-activated ion channels by itself (12, 13). The wealth of structural and functional information about these channels offers an opportunity to examine their modulation by Ca²⁺-CaM more closely. We report here experiments on the olfactory channel to define the site where Ca^{2+} -CaM binds as well as the molecular nature of the modulation. We have identified a domain on the channel protein that contributes to high apparent ligand affinity. When Ca²⁺-CaM binds to the same general domain, the influence of the domain is removed, leading to a decrease in apparent affinity for ligand. We also discovered that the NH2-terminus of the olfactory channel affects gating.

Identification of the CaM binding site. Our previous work indicated that the homo-oligomeric channel formed by the α subunit of the rat olfactory cyclic nucleotide–activated channel (which we call the olfactory channel) is strongly modulated by Ca²⁺-CaM (6). At the same time, the α subunit of the rod guanosine 3',5'-monophosphate (cyclic GMP)–activated channel (which we call the rod channel) neither

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