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Raman Spectroscopy of Argon Dimers

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The first experimental observation of van der Waals molecules by means of Raman scattering is presented. Ground-state rotational and vibrational spectra of dimers of argon were observed in a supersonic expansion. A dipole–induced-dipole model for the dimer polarizability could accurately reproduce the spectra. With use of a seeded expansion the value of the controversial dimer-to-monomer ratio was directly determined as 0.020(4).

In recent years van der Waals–bound molecules have been the subject of intense research efforts. Their internal properties have been studied by a number of techniques such as laser-induced fluorescence, uv absorption, mass spectroscopy, ir absorption, etc.[1] As a result of the extremely weak signal and small frequency shifts they have never been detected by Raman scattering.[2] This would make possible the direct determination of the rotational-vibrational properties of the ground-state molecule. Indeed, as Weber observed,[3] detection of resolved rotational Raman spectra of van der Waals–bound dimer molecules would constitute a major advance in sensitivity and resolution in Raman spectroscopy. Here, we present the first such spectra of argon dimers. In resolving the rotational spectra for the $v = 0$ vibrational state, we also observed hot rotational bands associated with higher vibrational states. In addition we have observed the vibrational bands. Since these transitions are about 100 times weaker than the rotational transitions, no attempt was made to resolve the rotational structure, as this pushes the limits of our instrumental sensitivity and stability.

A number of experimental reasons have retarded the observation of Raman dimer spectra. First, the intensity is proportional to the dimer density which is at most a few percent of the monomer density. At moderate pressures and temperatures collisional broadening smears out the spectrum which, in addition, is masked by a large background due to collision-induced light scattering. These collisional effects can be suppressed by a reduction in density and temperature.[4] The scattering intensity per dimer is weak since this depends on the square of the anisotropy of the dimer polarizability, which for the rare gases arises mainly from a dipole–induced-dipole mechanism. Finally, the spectra are in the vicinity of the laser frequency and suffer from interference due to Rayleigh and parasitic scattering.

To avoid the collisional problem we produced the dimers in a supersonic expansion which was used earlier to study monomers.[5] This has the additional advantage that substantially lower temperatures can be achieved than the liquefaction temperature of argon, thus simplifying the spectra and their interpretation. From our spectra we could determine both the temperature and the absolute density of the dimers in the expansion.

Determination of the concentration of van der Waals molecules in molecular beams by mass-spectroscopic techniques has been a long-standing problem due to uncertainties in ionization and fragmentation probabilities of the van der Waals molecules. Estimates of the dimer fractions vary by about one order of magnitude.[6] The Raman scattering technique does not suffer from the problems above. By seeding the expansion with N_2, which appears not to affect the Ar condensation, we could compare the N_2 and Ar_2 intensities to determine the dimer concentration.

In order to obtain a large Raman signal we used a crossed intracavity laser-expansion geometry (see Fig. 1), somewhat modified from our earlier design which used a focusing lens.[5] The laser cavity was formed by three mirrors in a folded configuration to produce a focus of 10-μm diam crossing the expansion axis at right angles. An intracavity power of order 50 W was achieved. An optional intracavity etalon narrowed the 5-GHz laser linewidth down to about 0.5 GHz, at the expense of a factor of 2 in power. The sonic nozzle, which was operated at room temperature, had a diameter of 140 μm and had xyz translation adjustments. Maximum pressures of 10 atm were used and the gas was pumped by a Roots pump. Since no skimmer was used the expansion could be probed upstream of the Mach disk.

Raman-scattered light was collected at right angles to both the laser and expansion axes. High resolution was obtained by using a Burleigh RC-10 Fabry-Perot etalon that was driven and actively stabilized with an on line PDP-11 computer. This was scanned in tandem with a Jobin-Yvon HG2S grating spectrometer which served to reject the large interfering Rayleigh signal. A direct optical path, circumventing the Fabry-Perot etalon and thus reducing losses, was used for the weaker vibrational spectra. The etalon was operated with a free spectral range of 6.9 cm^{-1} and finesse ~ 75. Resolution was 0.09 cm^{-1} with the intracavity etalon and 0.18 cm^{-1} without it. A cooled ITT FW130 photomultiplier with a 0.8-Hz dark count was used along with digital photon counting. Spectra were stored and averaged by the computer. The system was stable for about 20 h, being limited by a deterioration of the intracavity power. A high-resolution run required about 1 h/cm^{-1} measurement time. All spectra were recorded on the Stokes side of the laser line.

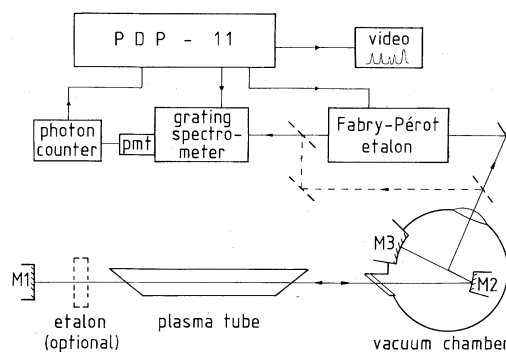A low-resolution spectrum of Ar_2 is shown in Fig. 2(a). This was measured for $X/D \simeq 2$ where

FIG. 1. A schematic of the crossed-beam system. The expansion nozzle (not shown) is centered in the vacuum chamber with its axis pointing out of the page.

D is the nozzle diameter and X the distance between the nozzle opening and the laser focus. Just beyond this point the dimer signal decreased below measurable values, in part because of massive condenstation into large clusters which presumably consumes the dimers (this will be discussed in a future article). For frequency shifts larger than 8 cm^{-1} no signal was observed, while for shifts smaller than 2.2 cm^{-1}, detection of dimer lines was not possible because of the strong laser interference. The first clearly resolved Raman line is the $J = 12 \rightarrow 14$ transition. The next line in the spectrum corresponds to a Raman transition $J = 14 \rightarrow 16$ and so on. (Since ^{40}Ar has zero nuclear spin the Ar_2 molecule in its ground electronic state $^1\Sigma_g^+$ can only occupy even J rotational states.) Using the energy levels given by Colbourn and Douglas[7] for the ground vibrational state (rotational constant $B = 0.0578$ cm^{-1}), we can reproduce the peak positions in the spectrum to within the experimental uncertainty. A high-resolution scan of part of the spectrum is shown in Fig. 2(b) and compared to a synthesized spectrum of the same resolution (dotted curve). This theoretical spectrum was calculated by numerically solving the radial Schrödinger equation for the HFD-C Ar-Ar potential.[8] The point dipole-induced-dipole model[9] was used to calculate the polarizability matrix elements and a spectrum was generated. (Although Frommhold and Bain[10] have carried out such calculations, we found their results to be in error by a factor of 3 and therefore decided to reproduce the entire calculation.) The main peaks are primarily due to molecules in the ground vibrational state. The spectrum shows a substructure due to the overlapping of the pure rotational bands arising from molecules in excited vibrational states with a slightly smal-
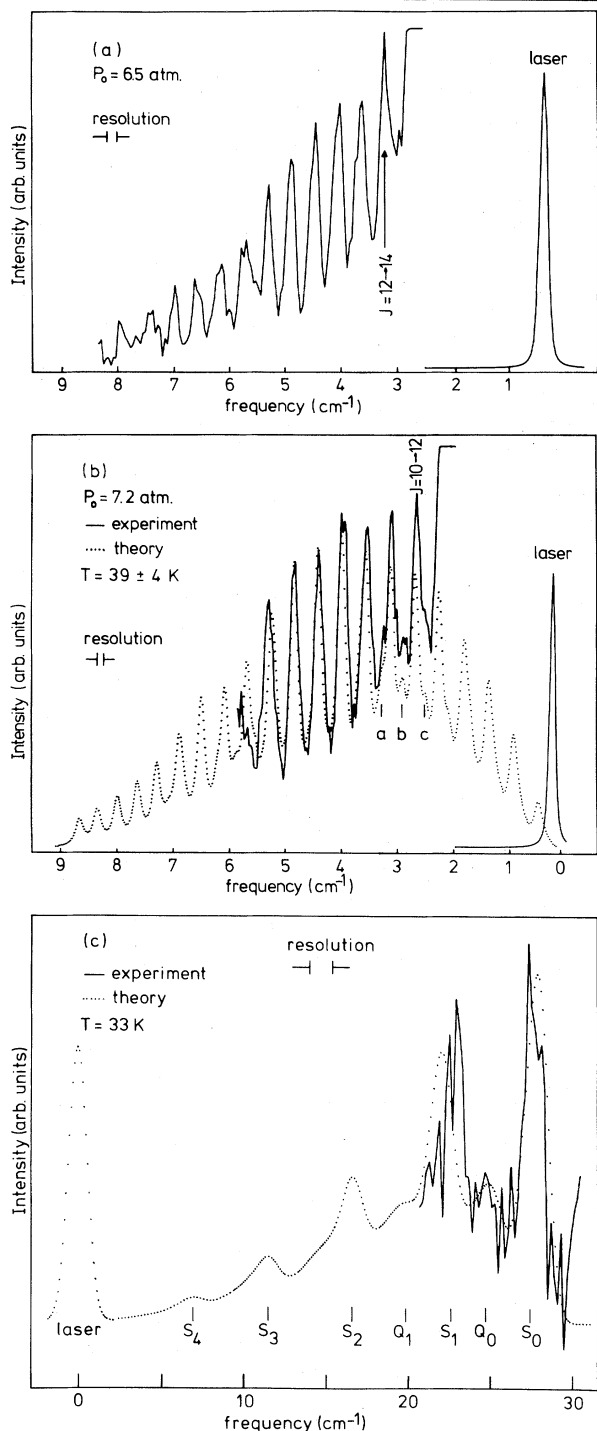
FIG. 2. (a) A low-resolution Raman spectrum of the Ar$_2$ pure rotational transitions. (b) A high-resolution spectrum showing "hot" (v = 1) rotational transitions which can be distinguished due to the large difference in rotational constant, B, for the v = 0 and 1 states. Note the comment, Ref. 11. (c) Low-resolution rotation-vibration spectrum over a limited frequency range. Intensities are about a factor of 100 smaller than in (a) or (b).

ler rotational constant. Peaks identified a, b, and c arise from the v = 1 vibrational state which lies about 40 K above the ground vibrational state. Agreement between theory and experiment is to within experimental uncertainty, if the rising background in the experiment (due to the laser) is taken into account.[11] The dimer temperature at X/D = 2 was determined to be 39 ± 4 K, if one assumes a Boltzmann distribution over both vibrational and rotational states. This is to be compared with the expected value of 35 K for an isentropic expansion.

In Fig. 2(c) we show a synthesized vibration-rotation spectrum and a part of the spectrum which we have measured. The signal here is about 100 times weaker than the rotational spectrum and is measured in low resolution (without the Fabry-Perot etalon). The peaks in the theoretical spectrum are due to unresolved Q and S branches. The subscripts indicate the initial vibrational quantum number v, with Δv = 1. Experimentally, O branches are expected to be smeared out so as to give no observable peaks. Contributions from transitions with $\Delta v > 1$ were calculated to be negligible. In view of the success of the dipole–induced-dipole model in predicting the rotational spectrum, the discrepancy in the peak position of the S_1 branch is puzzling.[12]

In a series of runs the Ar expansion was seeded (mixed) with ~ 4% N$_2$ (details will be discussed in a forthcoming article). This was used to deter-
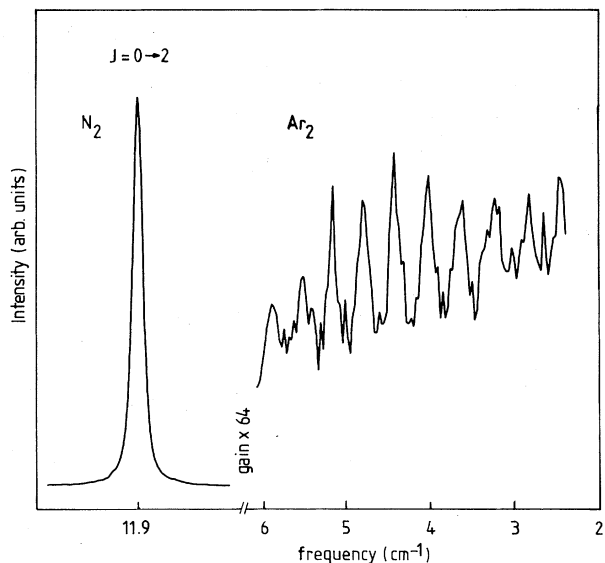

FIG. 3. Rotational spectrum for an N$_2$-seeded expansion used for determination of temperature and dimer/monomer fraction.

mine (a) the temperature in the expansion throughout our range of X/D and (b) the dimer concentration. Temperatures were determined from the rotational Raman spectrum of N_2 and were in agreement with those found from the Ar_2 spectrum. The Ar_2 concentration was determined by relating the intensity of dimer transitions with that of the simultaneously measured N_2 $J = 0 \rightarrow 2$ transition, shown in Fig. 3. Seeding with N_2 did not appear to affect the expansion properties. At a stagnation pressure $P = P_{Ar} + P_{N_2} = 5.95$ atm and a value of $X/D = 2$ the dimer density was found to be $1.5(3) \times 10^{17}/cm^3$. Under the assumption of an isentropic expansion with a flat sonic plane the dimer fraction is then determined to be $0.020(4)$. Scaling this result to the conditions that prevail in molecular-beam experiments would be rather difficult. In those experiments massive condensation, such as we observe, is usually avoided. However, our result probably sets an upper limit to the dimer fraction obtainable in molecular beams.

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