

Intracavity Far Infrared Laser Spectroscopy of Supersonic Jets: Direct Measurement of the Vibrational Motions in van der Waals Bonds

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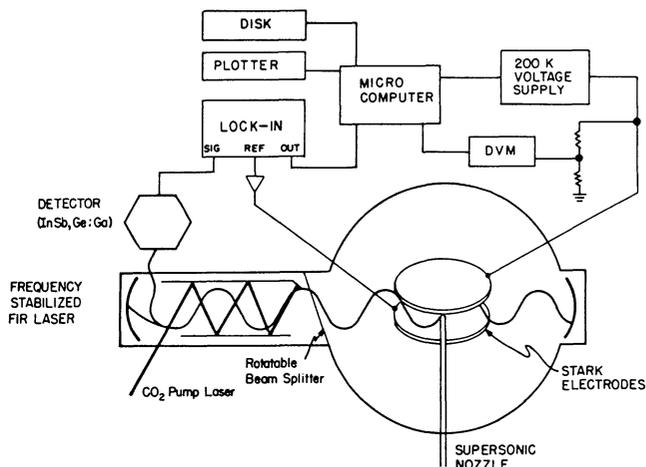
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Molecules held together by van der Waals forces generally possess bond strengths which are ~ 0.1 - 1.0% of normal chemical bonds, i.e. 0.1 - 1.0 Kcal/mole ($.35$ - 350 cm^{-1}). Such extremely weak bonds exhibit vibrational frequencies which lie in the far-infrared, eq. 10 - 100 cm^{-1} (1000 - 100 μm). In order to measure vibration-rotation spectra of van der Waals bonds, one must devise a method which possesses very high sensitivity in this region of the spectrum, and which preferably also has very high resolution capabilities, such that the hyperfine interactions, which can provide important information on the potential surface of these clusters, can be resolved. In this paper we report the development of such a new spectroscopic technique for directly measuring vibrational absorption spectra of van der Waals bonds. In this method, van der Waals molecules are produced in a supersonic free jet expansion located inside the optical cavity of an optically pumped far infrared laser. Electric field tuning of dipole-allowed vibration-rotation transitions into coincidence with the laser frequency produces an extremely sensitive detection method which also possesses very high (~ 1 MHz) resolution. We shall describe this new technique and its initial application for the measurement of the bending (ν_2) vibration in ArHCl near 34 cm^{-1} .

A schematic diagram of the spectrometer, is given in Figure 1. An optically pumped far infrared laser is the radiation source; by pumping ~ 60 different molecules with the lines from a CO_2 laser, approximately 2000 discrete frequencies can be obtained throughout the range 10 - 200 cm^{-1} . The high finesse ($f \approx 100$) optical cavity is divided into a gain cell and a sample region by a rotatable polypropylene beam splitter placed at the Brewster angle; the gain cell contains two parallel mirrors which are used to multipass the CO_2 pump laser in a transverse configuration, and an output coupler, which directs a portion of the laser radiation into a cryogenic Ga:Ge or InSb detector. The sample region consists of a large vacuum chamber pumped by a 10 " diffusion pump and contains a pair of 56 cm diameter polished aluminum electrodes and mounted to be parallel with a set of 5.0 cm Macor spacers. One of the electrodes is connected to a programmable power supply, which is swept from 0 to 100 kV, while the other is connected to an audio oscillator, amplifier, and transformer combination which can provide modulation voltages up to 1 kV at frequencies up to 100 kHz. The DC voltage is controlled by a microcomputer system, and is measured with a voltage divider and digital voltmeter. With this configuration, electric fields as high as 20 kV/cm are produced with high homogeneity and measured with an absolute accuracy of 0.02% . Both the far infrared laser and the CO_2 pump laser are locked to the cavity of the FIR laser for suitable frequency stability.

A $1/4$ " Pyrex tube with the tip drawn to a 10 - 100 μm orifice serves as a supersonic nozzle, which is inserted into the center of the electrodes

Fig. 1



INTRACAVITY FAR-INFRARED LASER STARK SPECTROMETER

through an XZ translation stage. Typical backing pressures employed range from 1 to 10 atmospheres, which result in pressures up to 1 mTorr in the vacuum chamber, above which dielectric breakdown becomes incapacitating. With this supersonic free jet configuration, Mach numbers as high as 3³ can be achieved, yielding average total number densities near 10^{16} cm^{-3} and translational temperatures near 10°K in the region of the intracavity FIR laser beam. Absorption of the intracavity laser radiation by vibration-rotation transitions in van der Waals molecules produced in the supersonic expansion are demodulated by a lock-in amplifier, and displayed as a function of the electric field strength.

We have observed extensive far infrared spectra of ArHCl in several of the regions where transitions are predicted^{1,2} to occur. Typical examples are presented in Figures 2 and 3, which are assigned to Stark-hyperfine components of Q(1) of the bending fundamental. Optimization of the experimental conditions (3% HCl in Ar, 6 atm backing pressure) produced signal-to-noise ratios as high as 10^4 for the 35 cm^{-1} transitions. Moreover, because the signals were measured in the intracavity configuration, saturation dips could readily be observed. Approximately 120 transitions have been measured in this region and assigned to Q(1), Q(2), and R(0) components. A preliminary least squares analysis of these transitions yields values for the ArH³⁵Cl rotational constant, ℓ -type doubling constant, dipole moment, and axial and perpendicular quadrupole coupling constants for the first excited bending state, and for the band origin of the bending vibration, which are given in Table 1. While a large number of transitions have been observed in the region where the parallel bending (24 cm^{-1}) and the stretching vibrations (33 cm^{-1}) are predicted to occur, detailed assignments and analyses of these have not yet been achieved. Similarly, a detailed analysis of spectra belonging to ArH³⁷Cl isotope has not been carried out at this time.

Interpretation of the spectroscopic information presented in Table 1 indicates that the average bending angle (of the HCl bond relative to the A inertial axis) increases from 41.2° in the ground state³ to nearly 76° in the first excited bending state. Because the dipole moment of the ArHCl molecule is essentially the projection of the HCl dipole onto the

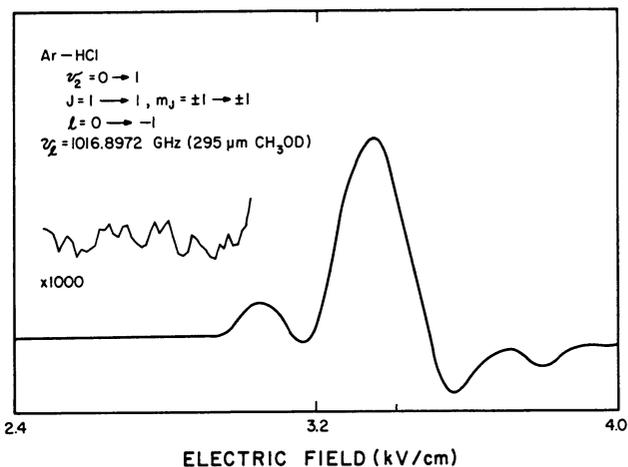


Fig. 2. High Sensitivity Spectrum Showing Signal-to-noise ratio of $>10^4$

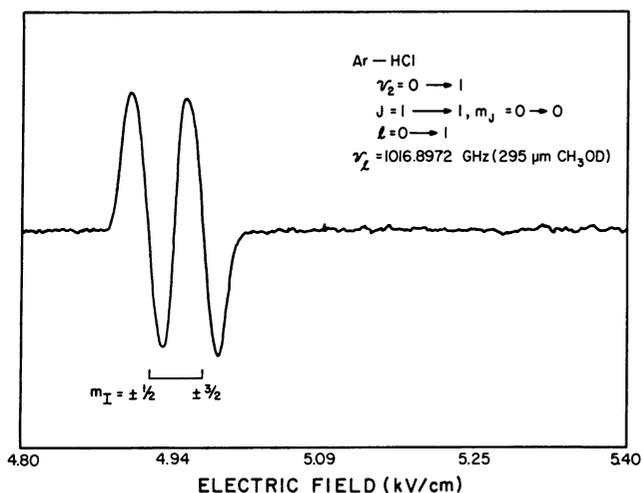


Fig. 3. High-Resolution Spectrum Exhibiting Resolved Hyperfine Splitting

Table 1. Effective Parameters for the $\nu_2 = 1$ State of ArHCl

$$\begin{aligned}
 B &= 1707.0(2) \text{ MHz} \\
 \nu &= 33.98127(1) \text{ cm}^{-1} \\
 q &= -50(3) \text{ MHz}
 \end{aligned}$$

$$\begin{aligned}
 eqQ_a &= 10(2) \text{ MHz} \\
 eqQ_b - eqQ_c &= -75(2) \text{ MHz} \\
 \mu &= 0.267(1) \text{ D}
 \end{aligned}$$

symmetry axis, excitation of the bend clearly produces a large dipole derivative, partially accounting for the very large signals observed for these transitions. Similarly large bending transitions moments are likely to occur quite generally for weakly bound molecules, as a result of the

large amplitude motions they undergo. Moreover, although the stretching vibration should, by analogy, produce a relatively small dipole derivative in these molecules, a very large Coriolis coupling between the van der Waals stretching and bending vibrations is indicated by the anomalously large ℓ -type doubling constant; hence, intensity borrowing from the bend should make van der Waals stretches generally accessible by direct absorption spectroscopy as well. One of the most interesting short-term prospects for these experiments is the probable assignment of many of the transitions observed near 25 cm^{-1} to the parallel bending vibration ($\Delta\ell = 0$). This transition correlates to the bending overtone ($\Delta v_2 = 2$) in the high anisotropy limit, but will actually occur at lower frequencies than the perpendicular bend ($\Delta\ell \pm 1$), which correlates to the fundamental ($\Delta v_2 = 1$), when the potential surface exhibits two attractive wells^{1,2}. Assignment of the 25 cm^{-1} transitions to the parallel bend would constitute the first experimental confirmation of the secondary minimum at ArClH configuration if this simple desorption is applicable to the potential surface.

Finally, we wish to point out that the simultaneous development of far-infrared laser-molecular beam electric resonance techniques by the Klemperer group at Harvard University constitutes a powerful complimentary technique for the study of vibrational spectra of van der Waals molecules. The combination of these two new approaches to the study of van der Waals bonding should add considerably to our knowledge of this important phenomenon over the next several years.

Acknowledgements

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