

ROTATIONAL SPECTRA OF SILANE COMPLEXES

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Recently we have studied the microwave spectra of argon-silane and silane-water complexes using a Fourier transform microwave (FTMW) spectrometer. For the main isotopic species, Ar- $^{28}\text{SiH}_4$, two $K = 0$ (A and F symmetry) and three $K = 1$ (E and F' symmetry) sets of rotational lines were observed at the rotational temperature of 1K by the supersonic expansion. In contrast, Ar- $^{28}\text{SiD}_4$ gave two $K = 0$ (A and F symmetry) and only two $K = 1$ (E and F' symmetry) rotational lines. Comparison of the rotational constants of Ar-SiH $_4$ with those of Ar-SiD $_4$ indicated that the contribution of the Coriolis coupling terms to the rotational constant of Ar-SiD $_4$ was twice as large as that of Ar-SiH $_4$.

In the case of SiH $_4$ -H $_2$ O, we have found that the two component molecules were surprisingly tightly bound each other, quenching their motions in the complex to a large extent except for the internal rotation. The binding of the two species seems to be much stronger than that by the van der Waals interaction and quite different in character from the hydrogen bonding; it is new in nature. The absence of the 1:3 intensity ratio in the present case indicates that the rotation of the water in the complex is largely quenched. The $A F E$ structure,^{a,c} which characterizes the spectra of a complex containing a tetrahedral molecule as a constituent, is not discernible in the spectra of the SiH $_4$ -H $_2$ O complex. The observed spectra may be interpreted as a case of a low internal rotation potential barrier V_3 when the C_2 axis of the water is bent away from the internal-rotation axis, which is probably quite close to the Si-O bond.

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Rotational REMPI Spectroscopy of the Hydrogen Halides

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Abstract

Wealth of spectroscopic data have been derived on electronically excited states of the hydrogen halides by conventional single photon spectroscopic methods. However, only limited information have been obtained on the rotational structure by these means.

Resonance enhanced multiphoton ionization (REMPI) spectroscopy, on the other hand, has proved to be more successful technique in this respect. Largest amount of information have been obtained on HCl, while a limited data are available on HBr and HI. Rotational spectroscopic constants have been derived for number of Rydberg states and for the $V(^1\Sigma^+)$ ion-pair states for HCl, HBr and HI. Most of these spectroscopic information have been derived from analysis of spectra recorded under jet cooled conditions, restricting its validity to low rotational energies. Rotational- and vibrational- perturbations due to state interactions have been observed in high resolution REMPI spectra of HCl and HBr. Thus intensity-, line width- and / or line position- anomalies have been observed in spectra of Rydberg- and / or ion-pair states of HCl and HBr.

In this paper we present rotational REMPI analysis of the $E(^1\Sigma^+)$ Rydberg state and the $V(^1\Sigma^+)$ ion pair state for $H^{35}Cl$, $H^{37}Cl$, $H^{79}Br$, $H^{81}Br$ and HI. Spectra were recorded at room temperature and analysed by simulation calculations in order to derive information i) -on spectroscopic parameters, ii) - on state interactions, as well as iii) - on the resonance excitation processes.

NOVEL, HIGH SENSITIVE INTRACAVITY-JET MILLIMETER WAVE SPECTROMETER

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A new intracavity-jet millimeter wave spectrometer was developed in order to measure with high accuracy extremely weak spectral lines of molecules and molecular van der Waals complexes, which possess small dipole moments or exhibit low abundances. The molecular jet expands into the high quality ($Q = 10^4$) resonator of a tunable coherent radiation source Orotron (106–150 GHz).¹ The absorption inside the cavity is detected by the variation of the electron current in the collector circuit of the Orotron. The simple method of detection and the high spectral purity of the source (10–15 kHz), which is achieved without any frequency or phase stabilization, make the spectrometer very efficient in searching for new weak absorption lines. The large effective length of the absorption path results in an improvement of sensitivity for more than a factor of 100 in comparison with the existing single pass schemes.² The entire system was tested by employing different molecules such as CO and its rare abundant isotopomers, and molecular complexes Ar-CO, Ne-CO and N₂-CO. The description of the spectrometer and the analysis of the data will be presented.

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STUDIES OF NO₂ BY LIF AND BOLOMETRIC DETECTION

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The visible and near-infrared spectrum of NO₂ is very dense and moreover the linepositions and intensities do not seem to follow any recognisable pattern. The conical intersection of the potential energy surfaces belonging to the electronic groundstate of ²A₁ symmetry and the first electronically excited ²B₂ state ^a, and the concomitant strong vibronic interactions, are held responsible for the intricate spectral structure.

The vibronic levels above the conical intersection are mixtures of low vibrational levels of the electronically excited state and high vibrational levels of the electronic ground state, causing an apparently chaotic frequency distribution of these hybrid states ^b in the spectral region above 16,000 cm⁻¹.

In a contribution towards a better understanding of the nature of the vibronic interactions in NO₂, we have investigated the region between 10,000 cm⁻¹ to 15,000 cm⁻¹, starting just above the conical intersection, by exciting a supersonically cooled beam of NO₂ molecules with a Ti:Sapphire ring laser ^c. The detection takes place by means of a photomultiplier or a bolometer. In this manner we can resolve the lines up to the hyperfine structure. Running spectra with this resolution was only feasible on the basis of previous measurements of vibronic band positions, in particular by Jost and coworkers ^d.

The hyperfine splitting in NO₂ is mainly due to the Fermi-contact interaction, which will vanish in a spin-restricted one-determinant description of a pure ²B₂ excited state. So the determination of the hyperfine splitting of the hybrid state, and its deviation from the ground state value, is a direct measure of the composition of the hybrid state.

The determination of A and B rotational constants, where possible, gives complementary information about a particular vibronic state.

The results for several vibronic bands are compared with calculations of the vibrational decomposition and assignments by Leonardi and Petrongolo ^e, and are in line with the trends found or predicted by these authors.

In future work we envisage to include a larger number of vibronic bands in order to strengthen the basis on which the assignments of transitions at higher energies can be made.

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IR PREDISSOCIATION SPECTRA OF $\text{CH}_3^+ \text{-Ar}_n$ COMPLEXES

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Mid-infrared spectra of mass selected $\text{CH}_3^+ \text{-Ar}_n$ ($n=1-8$) ionic complexes have been obtained by means of photofragmentation spectroscopy in a tandem mass spectrometer. Spectra of the dimer have been recorded in the vicinity of the first CH stretching overtones ($2\nu_3$, $2\nu_1$, $\nu_3 + \nu_1$) and their rotational structure is consistent with a pyramidal C_{3v} equilibrium geometry where the Ar atom is attached to the empty electrophilic $2p_z$ orbital of the C atom. Ab initio calculations (at the MP2 level) confirm this interpretation and predict a high binding energy of about 0.5 eV, resulting from partial charge transfer from Ar into the vacant $2p_z$ orbital. The rotationally resolved ν_3 spectrum of the $\text{CH}_3^+ \text{-Ar}_2$ trimer indicates that the two Ar atoms are located on opposite sides of CH_3^+ on the C_3 axis, however with significantly differing C-Ar bond lengths. Observed splittings are attributed to an intracuster tunneling motion between two equivalent C_{3v} minima via a symmetric D_{3h} transition state. Frequency shifts in the ν_3 vibrational spectra of larger clusters ($n \geq 3$) suggest that further Ar atoms are weakly attached to the trimer, which acts as the effective nucleation center for the cluster growth.

THE INTERMOLECULAR VIBRATIONS OF THE NO DIMER

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The propensity of the NO radical to dimerize has long been known. From pure rotational¹ and infrared² spectra, we know that (NO)₂ is a planar C_{2v} molecule with an N-N distance of about 2.26 Å and a singlet ground electronic state. One mystery of the NO dimer involves the nature and location of the many other dimer electronic states (both singlet and triplet) that are formed by bringing together two NO monomers. Another mystery involves the locations of the four low frequency (intermolecular) vibrational modes of the dimer, which have never been observed in the gas phase before.

We have now solved the second mystery by means of observations with a long-path (180 m), low-temperature (100 K) absorption cell and a Bomem FTIR spectrometer in both the mid- and far-infrared regions. This is the first observation of the gas-phase far-infrared spectrum of the NO dimer. The a₁ vibrations ν₂ (symmetric bend) and ν₃ (intermolecular stretch) have been assigned at 239.36 and 134.50 cm⁻¹, respectively. The very weak ν₆ (b₂ asymmetric bend) fundamental band is located at 429.14 cm⁻¹, and the infrared forbidden ν₄ (a₂ torsion) vibration is at about 117 cm⁻¹.

These values for the intermolecular modes of (NO)₂ agree poorly with previous "accepted"³ values based on spectra of condensed NO or matrix-isolated NO dimer.⁴ However, they are consistent with a force field which we had derived⁵ from centrifugal distortion parameters. Accurate calculations on the NO dimer pose a considerable challenge for quantum chemistry, but our CCSD(T) calculations are in reasonable qualitative agreement with the experimental values, and they indicate that there are no other stable isomers of (NO)₂.

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