High resolution IR spectroscopy of van der Waals complexes as prototypes of molecular clusters

Michio Takami

Inorganic Chemical Physics Laboratory

Van der Waals dimer complexes containing spherical top molecules (SF_6 and SiF_4) are studied by high resolution IR spectroscopy as prototypes of molecular clusters. The $(SF_6)_2$ and $(SiF_4)_2$ complexes have D_{2d} and D_{3h} symmetry, while all SiF_4-X (X = Ar, Kr, CO, N_2) complexes have C_{3v} symmetry. Unique structures and dynamics of these complexes are discussed.

Spectroscopic study of vdW dimers is of particular interest as prototypes of molecular clusters. We have chosen spherical top molecules (T_d and O_h) as constituents of the complexes. Although a spherical top molecule is regarded as a special type of symmetric top molecules ($A = B$), its ro-vibrational spectra are far more complex because the degeneracy of all K states produces higher order splitting. In a dimer complex, however, the bonding lowers the symmetry from T_d or O_h to C_{3v}, D_{2d}, or C_{2h}, and in principle the spectra should become much simpler by the removal of the K degeneracy. The experimental results showed far more complex features against this expectation.

Van der Waals dimers were produced by diluting relevant sample gas into about 7 atm. rare gas (He, Ar, Kr) with 0.5–5% concentration, and expanding the mixed gas into vacuum through a pulsed nozzle with 0.5 mm diameter orifice. The IR absorption spectra were measured with several frequency tunable infrared diode lasers. Transient infrared absorption signals were averaged by Boxcar Integrators and stored in a computer.

A parallel band of $(SF_6)_2$ is shown in Fig. 1 as an example of the spectra.[1] This band is 13.97 cm^{-1} redshifted from the monomer band origin. A well resolved J-structure indicates that the molecule is a symmetric top. From the intensity distribution of the lines, rotational temperature of the complex
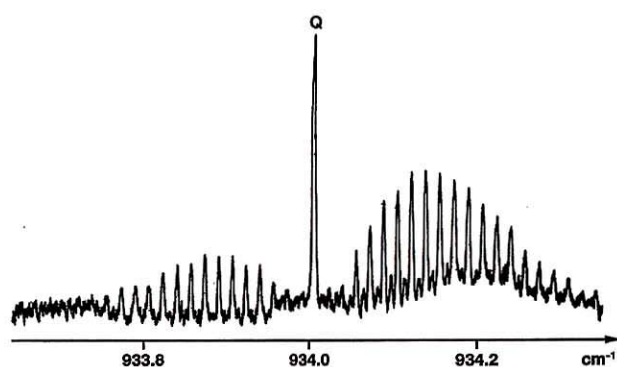
was estimated to be about 1 K. A perpendicular band was observed with 8.12 cm^{-1} blueshift from the monomer band origin, and showed partly resolved K structure with nearly equal spacing. Spectroscopic parameters were determined by simultaneous analysis of the two bands by assuming that the complex was a symmetric top. The structure of this complex was determined to be D_{2d} (see Fig. 2(a)) from the perpendic-

Fig. 1. High resolution IR absorption spectrum of the parallel band of $(SF_6)_2$.
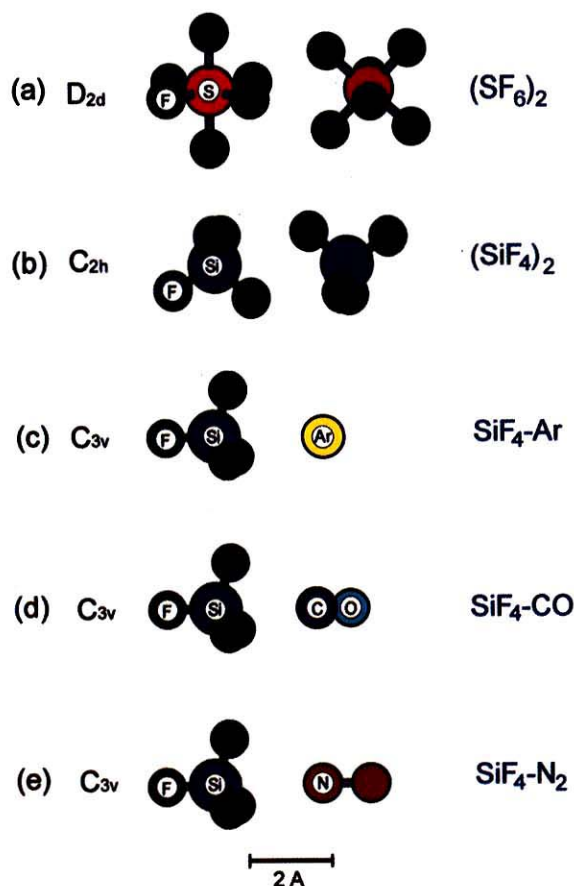

Fig. 2. The structures of studied complexes. Atomic distances are accurate within 5%. Note that there are 288 structural isomers in the D_{2d} structure.

ular band which shows a clear strong-weak intensity alternation in the K structure accompanied with first-order Coriolis interaction. In this structure, there exist $12 \times 12 \times 2 = 288$ structural isomers corresponding to the combination of twelve F-F ridges for each SF_6 and two relative positions of the two ridges facing each other. A tunneling motion among different isomers removes the 288-fold degeneracy and produces 17 sublevels with the degeneracy of 1, 9, 12, or 55. If the barrier for the tunneling is reasonably high and the splitting is on the orders of a few cm^{-1}, there should appear many hot bands from these sublevels at about 1 K internal temperature of the complex. The observed parallel and perpendicular bands are accompanied with many weak bands, suggesting the possibility of such tunneling motion. Unfortunately, these bands have not been analyzed yet because they are too weak and rotational lines are not well resolved.

The $(SiF_4)_2$ complex shows spectra[2] similar to those of $(SF_6)_2$ but with a clear difference. A unique feature of this complex is the appearance of two perpendicular bands with no first-order Coriolis interaction. This unusual observation is consistent only with the C_{2h} structure shown in Fig. 2(b). In this structure, there exists only two-fold rotational symmetry along the Si-Si axis. Therefore, this complex is not a symmetric top by definition because a symmetric top is defined by the presence of higher than two-fold rotational symmetry along the symmetry axis. However, the observed band structures are very similar to those of a symmetric top except that there are two perpendicular bands and there is no first-order Coriolis interaction. This is simply due to the fact that, although this complex does not have C_{nv} ($n \geq 3$) symmetry, two moments of inertia perpendicular to the Si-Si axis are exactly equal because the constituent molecules have spherical symmetry. This is the first example of a true (not nearly) *accidental symmetric top* molecule. The structure of this complex cannot be determined uniquely from the experimental data because the angle between the Si-Si axis and Si-F bond (facing to its counterpart) has no influence on the molecular parameters. An *ab initio* calculation[3] provided about $40°$ for this angle, suggesting that the structure is equilibrated by a subtle balance of an attractive force between Si and non-bonded F atoms with a repulsive force between F atoms.

All SiF_4-X complexes show one parallel and one perpendicular bands mostly on the red side of the monomer band origin.[4,5] By the formation of complex, first-order Coriolis interaction among the triply degenerate ν_3 state of SiF_4 now reduces to the first-order Coriolis interaction in the E state and a second-order A-E Coriolis interaction between the A and E states.[6] Since the A-E energy separation is very small in these complexes, the interaction strongly distorts both bands while one of the Q-branches of the perpendicular band is left unperturbed by symmetry, showing extremely strong and narrow line. The whole spectra were analyzed successfully by direct diagonalization of the interaction matrix. The structures were all C_{3v} where a rare gas atom or a diatomic molecule is bonded with Si atom (see Fig. 2(c)–(e)).

Another interesting observation is the energy difference between the A and E states for both types of complexes. For spherical top dimers, about 22 cm^{-1} splitting has been observed. This splitting occurs by a resonant dipole-dipole interaction, or in a semi-classical model, by a rapid exchange of vibrational quantum between the two identical units. This model predicts the shifts of the two bands from monomer origins by $-2(A) : 1(E)$. For $(SF_6)_2$, the calculated A-E separation agrees quite well with the experimental value ($< 2\%$) though the absolute frequencies are about 2 cm^{-1} redshifted. In $(SiF_4)_2$, the agreement is much worse. A similar splitting observed in SiF_4-X complexes are much smaller because it occurs by the dipole-induced dipole interaction. According to this model, shifts of the bands from the monomer origin should be $-4(A) : -1(E)$ with much smaller absolute values compared with those in resonant dipole-dipole interaction. The agreement with the experimental values are even worse because the modification of the force field by complexing dominates over the small induction effects. For SiF_4-CO and SiF_4-N_2, *ab initio* calculation of the vibrational frequencies is found to provide much better values.[5]

We have also recorded the spectra of CF_4-Ar, SiF_4-Ne, and SF_6-Ar. All these spectra show quite anomalous features and does not fit to any known rigid rotor spectra, indicating the presence of internal motion of the bonded rare gas atoms. Analyses of these spectra are the work left in future.

References
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