THE INFRARED PHOTODISSOCIATION SPECTRA AND THE INTERNAL MOBILITY OF SF₆⁻, SiF₄⁻ AND SiH₄⁻DIMERS

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ABSTRACT

We present an analysis of the couplings originating from different intermolecular interactions (electrostatic, exchange, dispersion, induction) which split and shift the frequencies of the vibrational transitions in Van der Waals dimers, and determine their intensities. Model potential calculations illustrate the importance of the various contributions in (SF₆)₂, (SiF₄)₂ and (SiH₄)₂ and their dependence on the monomer orientations. The results, in conjunction with calculated equilibrium structures, barriers to internal rotation and (harmonic) Van der Waals vibrational frequencies, lead to several observations which are relevant for the interpretation of the infrared photodissociation spectra of these complexes. We confirm that in (SF₆)₂ and (SiF₄)₂ (orientation-independent) resonant dipole-dipole coupling dominates the appearance of the spectra. For (SiH₄)₂ we conclude, however, that other than electrostatic terms are not negligible and, moreover, that the electrostatic coupling leads to orientation-dependent vibrational frequencies and intensities. This orientational dependence is related to the large displacements of the hydrogen atoms in the ν₄ mode of SiH₄. We also find that the internal rotations in (SF₆)₂ and (SiF₄)₂ are more strongly locked than those in (SiH₄)₂. Especially the geared internal rotations in the latter dimer could easily occur at the experimental molecular beam temperatures.

1. INTRODUCTION

The photodissociation of (SF₆)₂, (SiF₄)₂ and (SiH₄)₂ by means of CO₂ laser light in the frequency range from 880 to 1100 cm⁻¹ has been the subject of detailed experimental studies. In all these complexes the monomers have an infrared-active vibrational mode in this range: the ν₃ modes of SF₆ and SiF₄ at 948 cm⁻¹ and 1031 cm⁻¹, respectively, and the ν₄ mode of SiH₄ at 913 cm⁻¹. In the free monomers these modes are threefold degenerate; in the dimers their degeneracy is lifted. Photodissociation spectra have been obtained by irradiating a beam of dimers with a CO₂ laser and monitoring, by a mass spectrometer or by a bolometer, the changes in dimer concentration. These spectra show the frequency splittings of the monomer modes in the dimers, the intensities of the infrared allowed dimer transitions and the line widths of these transitions, which are related to the dimer predissociation life times. Additional information has been extracted from elegant two- and three-pump/probe laser experiments and from the resolution of the peaks originating from different S and Si isotopes.
Before we summarise the results of these studies, let us note that for none of these Van der Waals complexes the structure has been determined. In particular, it is not known whether the monomer rotations are (strongly) hindered in the dimers and, if they are, what the orientations of the monomers are. The following results emerge from the spectra. In isotopically homogeneous \((\text{SF}_6)_2\) and \((\text{SiF}_4)_2\) there are two peaks with an intensity ratio of nearly 1 : 2 which are shifted from the monomer \(\nu_3\) frequency by amounts \(\Delta \nu\) which have a ratio close to \((-2) : 1\). This can be explained by a splitting of the threefold degenerate monomer \(\nu_3\) mode due to resonant dipole-dipole coupling in the dimer. The two peaks correspond with the transition-dipole components of the coupled \(\nu_3\) mode that are parallel and perpendicular to the dimer bond axis, respectively. Also the further splitting of these two peaks in isotopically mixed \((\text{SF}_6)_2\) and \((\text{SiF}_4)_2\) dimers can be explained by the resonant dipole-dipole coupling mechanism. As shown below, the dipole-dipole coupling mechanism is equally effective for all orientations of the monomers and, so, the splitting of the monomer vibrational peaks in \((\text{SF}_6)_2\) and \((\text{SiF}_4)_2\) cannot be used to determine the monomer orientations.

In \((\text{SiH}_4)_2\) the threefold degenerate \(\nu_4\) mode splits into two peaks as well, but the intensity ratio and the shifts of these peaks from the monomer frequency are qualitatively different from the other dimers and cannot be explained by the resonant dipole-dipole coupling mechanism\(^4\). An attempt to add to this mechanism the effect of dipole-induced dipole interactions\(^5\) gave a slight improvement of the calculated results, but the experimental observations could still not be explained in a satisfactory manner. So in \((\text{SiH}_4)_2\) the mechanism which dominates the coupling between the resonant \(\nu_4\) transitions is yet uncertain.

Another question regards the line widths of the observed dimer peaks. The broadening of these lines is partly homogeneous, related to the vibrational predissociation lifetime, and partly inhomogeneous. Snels and Fantoni\(^4\) have tried to explain the inhomogeneous broadening by including rotational transitions of the monomers, which were assumed to rotate freely in the dimer, as well as dimer end-over-end rotational transitions. Hole burning experiments by Heymen et al.\(^6,7\) have separated the homogeneous and inhomogeneous line broadening effects and disproved the model of Snels and Fantoni\(^4\). The model invoked by Heymen et al. to explain these more recent experiments\(^7\) includes the centrifugal distortion associated with the dimer end-over-end rotation, as well as Coriolis interactions associated with internal monomer rotations. So, also in this model free internal rotations of the monomers are assumed. The conclusions do not critically depend on this assumption, however, since the most relevant Coriolis interactions actually arise from the simultaneous rotation of both monomers about the dimer bond axis. We think, therefore, that the question to what extent the monomer rotations are hindered in the dimer is still open.

The present study concerns the two main questions which remain after the analysis of the experimental data. First, we have derived which mechanisms, in addition to the resonant dipole-dipole interaction, may couple the infrared-active monomer vibrations in \((\text{SF}_6)_2\), \((\text{SiF}_4)_2\) and \((\text{SiH}_4)_2\) and lift the degeneracy of these vibrations. In this derivation we have started from an intermolecular potential which includes the electrostatic, exchange, dispersion and induction interactions. In order to estimate the relative importance of each coupling contribution we have replaced the potential by an empirical atom-atom potential, supplemented with induction terms. From this analysis it follows.
also how the splitting between the dimer vibrational peaks depends on the monomer orientations.

Secondly, we have calculated from the same potential the equilibrium structure of each of the Van der Waals dimers and estimated the barriers to internal rotation of the monomers. We have also estimated the frequencies of the Van der Waals vibrations by means of a harmonic analysis. These Van der Waals vibrations are not directly observed in the photodissociation spectra, but since they affect the monomer orientations and the distance between the monomers, they influence the positions and the widths of the observed dimer peaks.

2. VIBRATIONAL COUPLING

In order to demonstrate which mechanisms couple the monomer vibrations in \((\text{SF}_{6})_2\), \((\text{SiF}_4)_2\) and \((\text{SiH}_4)_2\) and, thereby, determine the photodissociation spectra of these dimers, it is convenient to model the intermolecular interactions by an atom-atom potential. Such a potential depends on the orientations of the monomers and, thus, it gives an idea to what extent the monomers are free to rotate in these Van der Waals complexes. It also depends (implicitly) on the monomer internal coordinates and, therefore, it yields all the terms that couple the monomer vibrations. An atom-atom potential between two molecules \(A\) and \(B\) is usually written as

\[
V_{AB} = \sum_{i \in A} \sum_{j \in B} \left[ A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6} + q_i q_j r_{ij}^{-1} \right],
\]

where the first term represents the exchange interactions, the second term the dispersion interactions and the third term the electrostatic interactions. The parameters in this potential are \(A_{ij}, B_{ij}, C_{ij}\) and the fractional charges \(q_i\) and \(q_j\) on the atoms \(i\) belonging to molecule \(A\) and the atoms \(j\) belonging to \(B\). For all these interactions it is common to assume pairwise additivity, as reflected by Eq. (1). The induction interactions, however, contain three-body terms which are equally important as the pairwise terms and we model them by

\[
V_{AB}^{\text{ind}} = -\frac{1}{2} \sum_{i \neq i' \in A} \sum_{j \in B} q_i q_{i'} \alpha_{ij} (\hat{r}_{ij} \cdot \hat{r}_{ij'}) r_{ij}^{-2} - \frac{1}{2} \sum_{i \neq i' \in A} \sum_{j \neq j' \in B} q_i q_{i'} q_j q_{j'} \alpha_{ij} \alpha_{ij'} (\hat{r}_{ij} \cdot \hat{r}_{ij'}) r_{ij}^{-2}.
\]

We have assumed here that the atomic polarizabilities \(\alpha_i\) and \(\alpha_j\) are isotropic and we have neglected the (higher order) interactions between the induced moments. The interatomic vectors \(\hat{r}_{ij}\) can be written as \(\hat{r}_{ij} = R + \hat{r}_i - \hat{r}_j\), where \(\hat{r}_i\) and \(\hat{r}_j\) denote the position vectors of the atoms \(i\) and \(j\) relative to the centers of mass of the molecules \(A\) and \(B\), respectively, and \(R\) is the vector that points from the center of mass of molecule \(A\) to that of molecule \(B\).

The dependence of the intermolecular potential \(V_{AB}\) on the intramolecular vibrational coordinates can be made explicit by writing it as a Taylor expansion in the atomic displacement coordinates

\[
u_i = \hat{r}_i - \hat{r}_i^{(0)}
\]

\[
u_j = \hat{r}_j - \hat{r}_j^{(0)},
\]
which we shall arrange in column vectors \( u_A \) and \( u_B \) with \( 3N_A \) and \( 3N_B \) components. \( N_A \) and \( N_B \) are the numbers of atoms in the molecules A and B, \( r_i^{(0)} \) and \( r_j^{(0)} \) the equilibrium positions of these atoms. Up to second order this expansion yields

\[
V_{AB} = V^{(0)} + V_A^{(1)} u_A + V_B^{(1)} u_B + \frac{1}{2} u_A^T V_{AA}^{(2)} u_A + u_A^T V_{AB}^{(2)} u_B + \frac{1}{2} u_B^T V_{BB}^{(2)} u_B \tag{4}
\]

The "static potential" \( V^{(0)} \) has the same form as Eqs. (1) and (2) with all the (instantaneous) interatomic vectors \( r_{ij} \) replaced by the equilibrium vectors \( r_{ij}^{(0)} = R + r_i^{(0)} - r_j^{(0)} \). Explicit expressions for the first and second derivatives \( V_A^{(1)} \) and \( V_B^{(2)} \), where \( X,Y = A \) or \( B \), are given in a forthcoming paper.\(^8\)

The splitting and shifts of the monomer vibrational frequencies are easily calculated if we first transform Eq. (4) to the normal coordinates \( Q_A \) and \( Q_B \) of (specific) intramolecular vibrations. The connection between the atomic displacements \( u_A \) and \( u_B \) and these normal coordinates is simply given by

\[
\begin{align*}
    u_A &= R_AL_A Q_A \\
    u_B &= R_BL_B Q_B.
\end{align*}
\tag{5}
\]

The matrices \( L_A \) and \( L_B \) can be calculated from the (harmonic) force fields of the free monomers by the standard GF-matrix method.\(^9\) The rotation matrices \( R_A \) and \( R_B \) depend on the orientations of the monomers in the dimer; they rotate the cartesian components of the atomic displacements with respect to the monomer frames to the corresponding components relative to the dimer frame. After this transformation Eq. (4) becomes:

\[
V_{AB} = V^{(0)} + W_A^{(1)} Q_A + W_B^{(1)} Q_B + \frac{1}{2} Q_A^T W_{AA}^{(2)} Q_A + Q_A^T W_{AB}^{(2)} Q_B + \frac{1}{2} Q_B^T W_{BB}^{(2)} Q_B \tag{6}
\]

with

\[
\begin{align*}
    W_A^{(1)} &= V_A^{(1)} R_X L_X \\
    W_B^{(1)} &= V_B^{(1)} R_Y L_Y \\
    W_{AA}^{(2)} &= L_X^T R_X R_A^T L_X \\
    W_{AB}^{(2)} &= L_X^T R_X R_B^T L_Y \\
    W_{BB}^{(2)} &= L_Y^T R_Y R_B^T L_Y
\end{align*}
\tag{7}
\]

for \( X,Y = A \) or \( B \).

If the monomer vibrations are assumed to be harmonic, it becomes fairly obvious how the coupling terms in Eq. (6) will affect their frequencies. Each of the vibrations we are interested in, \( \nu_3 \) in \( \text{SF}_6 \) and \( \text{SiF}_4 \), \( \nu_4 \) in \( \text{SiH}_4 \), is threefold degenerate in each monomer. Their components, which we denote by \( x, y \) and \( z \), span the irreducible representations \( T_{1u} \) and \( T_2 \) of the point groups \( O_h \) and \( T_d \), respectively. So in the non-interacting monomers we have six equivalent harmonic modes, which define the unperturbed states

\[
| n_{xA}, n_{yA}, n_{zA}, n_{xB}, n_{yB}, n_{zB} \rangle.
\]

In the ground state \( | 0 \rangle \) all these quantum numbers \( n \) are equal to zero. In the sixfold degenerate first excited state with components \( | x_A \rangle, | y_A \rangle, | z_A \rangle, | x_B \rangle, | y_B \rangle, \) and \( | z_B \rangle \) the quantum number \( n \) that corresponds to the mode indicated has been raised to \( n = 1 \). The splitting and shifts of the monomer fundamental vibrational frequencies can be calculated by taking Eq. (6) as the perturbation and using first order perturbation theory for the ground state and the degenerate first excited state of the dimer. The normal mode coordinates \( Q_A \) in Eq. (6) refer to the modes \( x_A, y_A \) and \( z_A \) and the
the molecular polarizabilities $\alpha_A$ and $\alpha_B$ by $\alpha_A = \sum_{i \in A} \alpha_i$ and $\alpha_B = \sum_{i \in B} \alpha_i$, this leading induction term adopts the form given in Ref. 5 and it contributes to the shifts of the vibrational frequencies as indicated there.

The splitting and shifts of the vibrational frequencies caused by the leading electrostatic (dipole-dipole) and induction (dipole-induced dipole) interactions appear to be independent of the monomer orientations. At first sight this seems surprising, since the matrices $W_{X_0}$ that determine the splitting and the shifts of the frequencies depend on the monomer orientations through the rotation matrices $R_A$ and $R_B$, see Eq. (7). It can be proved, however, that the rotations $R_A$ and $R_B$ just amount to a similarity transformation of the dynamical matrix in Eq. (8), when this matrix contains only the dipole-dipole and dipole-induced dipole couplings.

We can make a similar expansion of the exchange and dispersion contributions to the coupling matrices $V^{X_0}_{XY}$. They give rise to splitting and shifts of the vibrational frequencies which display a different pattern than obtained from the electrostatic interactions only. In general, the splitting and shifts caused by the leading exchange and dispersion terms depend on the monomer orientations. Also the effects of the higher electrostatic and induction terms on the vibrational frequencies depend on the monomer orientations.

The contributions of the various intermolecular interactions to the vibrational coupling in Van der Waals complexes have been calculated explicitly for $(\text{SF}_6)_2$, $(\text{SiF}_4)_2$ and $(\text{SiH}_4)_2$. To try and simulate the dimer vibrational spectra (see Section 4) in the frequency range from 880 to 1100 cm$^{-1}$, we have also calculated the infrared intensities of the dipole allowed transitions. We concentrate, in particular, on the dependence of the calculated spectra on the monomer orientations. In line with the atom-atom model used for the intermolecular potential, we write the following expression for the vibrational dipole moment operator of a dimer

$$\mu = \sum_{i \in A} q_i \mathbf{r}_i + \sum_{j \in B} q_j \mathbf{r}_j + \sum_{i,j} q_i \alpha_j r_{ij}^{-3} \mathbf{r}_{ij} - \sum_{i,j} q_j \alpha_i r_{ij}^{-3} \mathbf{r}_{ij}. \quad (11)$$

The first two terms are the vibrational dipole moments of the monomers $A$ and $B$, as represented by a model with fractional charges $q_i$ and $q_j$ assigned to the vibrating atoms. Actually we have chosen these charges such that the known transition strengths of the $\nu_3$ vibrations in $\text{SF}_6$ and $\text{SiF}_4$ and the $\nu_4$ vibration in $\text{SiH}_4$ are exactly reproduced. We have added to each monomer term the induced dipole moment caused by the (vibrating) charges on the other monomer. Substituting Eq. (3) into Eq. (11) and making a Taylor expansion, we find $\mu$ explicitly as a function of the vibrational atomic displacements $u_A$ and $u_B$. For calculating the transition strengths in the harmonic approximation we need only the first order expansion

$$\mu = \mu^{(0)} + \mu_A^{(1)} u_A + \mu_B^{(1)} u_B \quad (12)$$

where $\mu^{(0)}$ is obtained from Eq. (11) by replacing $r_{ij}$ by $r_{ij}^{(0)}$ and the first order coefficients are given in Ref. 8. Using Eq. (5) we obtain $\mu$ in terms of the normal coordinates $Q_A$ and $Q_B$ of the monomer vibrations

$$\mu = \mu^{(0)} + M_A^{(1)} Q_A + M_B^{(1)} Q_B \quad (13)$$
The transition strengths of the dimer excitations are given by
\[ T_{0\rightarrow 1} = | \langle 0 | \mu | 1 \rangle |^2 \] (14)
where \( | 1 \rangle \) is an eigenstate of the matrix given by Eq. (8). Substituting Eq. (13) for \( \mu \) and the appropriate linear combinations of monomer excited states for \( | 1 \rangle \) and using the standard harmonic oscillator algebra, we can easily calculate the transition strengths of all the vibrational transitions in the dimer.

If the excited states \( | 1 \rangle \) would simply be given by Eq. (9) and \( \mu \) is restricted to the first two terms in Eq. (11), then we obtain the well known result that the transitions to the minus-states in Eq. (9) are forbidden and those to the plus-states are allowed with equal intensities. This yields the characteristic spectrum with one peak at position \( \omega_0 + \Delta \) and another peak at position \( \omega_0 - 2\Delta \), and an intensity ratio of 2 : 1, that is obtained when only the electrostatic dipole-dipole interactions are included (\( \omega_0 = \omega_a + \omega_B \)). In general, the excited states \( | 1 \rangle \) from Eq. (8) are more complex, however. For arbitrary orientations of the monomers all dimer transitions become allowed, in principle, and their intensities become orientation-dependent, just as their frequencies.

3. VAN DER WAALS VIBRATIONS

Given the potential expansion in Eq. (4) it is relatively easy to calculate the Van der Waals vibrations of the dimers, in the harmonic approximation. Although we realize that the harmonic model will not be appropriate for the larger amplitude Van der Waals vibrations, it is still interesting to consider the harmonic frequencies and the corresponding normal modes, since these give already a clear indication of the extent to which specific monomer rotations will be hindered (see Section 4). First we find, by direct minimisation of \( V^{(0)} \), the equilibrium structure of the dimer, i.e. the equilibrium distance \( R \) and the equilibrium orientations of the monomers. Next, we use the second derivatives \( V^{(2)}_{AB}, V^{(2)}_{AA} \) and \( V^{(2)}_{BB} \) and we transform these as in Eq. (7). Instead of the matrices \( L_A \) and \( L_B \) that correspond to the normal modes of vibration \( Q_A \) and \( Q_B \) of the monomers, we use the matrices \( \tilde{L}_A \) and \( \tilde{L}_B \) that correspond to the Eckart coordinates for the center of mass translations and the overall rotations of the monomers. This yields a 12 dimensional force constant matrix with blocks \( \tilde{W}^{(2)}_{AA}, \tilde{W}^{(2)}_{AB}, \tilde{W}^{(2)}_{AB} \) and \( \tilde{W}^{(2)}_{BB} \) which, together with the appropriate inertia matrix that contains the molecular masses and moments of inertia, gives the 6 harmonic frequencies of the Van der Waals vibrations (and 6 frequencies zero that correspond with the overall translations and rotations of the dimer) and the corresponding normal modes.

One complication has yet been overlooked in this simple description. The space spanned by the linearized Eckart coordinates for the monomer rotations is not invariant under the overall rotations of the dimer. For rotational invariance of the dynamical problem it is necessary, and in the harmonic model sufficient, to include additional terms in the atomic displacements, Eq. (5), which are quadratic in the Eckart coordinates \( \tilde{Q}_A \) and \( \tilde{Q}_B \) of the monomer rotations. The transformation matrices occurring in these terms, which are derived in Ref. 11, must be multiplied with the first derivatives.
$V^{(1)}_A$ from Eq. (4), and be added to the diagonal blocks $\tilde{W}^{(2)}_{AA}$ and $\tilde{W}^{(2)}_{BB}$, as described in Ref. 12, for instance. Thus, the 3 eigenfrequencies of the 12-dimensional harmonic eigenvalue problem that correspond with the overall rotations of the dimer will indeed be zero. This correction affects the frequencies of the five rotational Van der Waals vibrations.

4. RESULTS AND CONCLUSIONS

In order to make more quantitative estimates of the various coupling terms derived in Section 2, which may affect the photodissociation spectra of $(SF_6)_2$, $(SiF_4)_2$ and $(SiH_4)_2$, we have substituted literature values for the parameters occurring in the atom-atom interaction potential, Eqs. (1) and (2), and in the vibrational dipole-moment operator, Eq. (11). Using these values, given in Ref. 8, we have first determined the equilibrium structure of each dimer by minimizing the "static" intermolecular energy $V^{(0)}$. The dimer structures are shown in Fig. 1. The effect of the electrostatic and induction interactions on the binding energies are small; we are dealing with real Van der Waals dimers which are bound mainly by the dispersion attraction. In general, the calculated dimer equilibrium structures depend rather sensitively on the atom-atom parameters chosen for the exchange and dispersion interactions. So, we have avoided drawing conclusions that depend too specifically on the equilibrium structure calculated.

In order to get some insight into the internal mobility of these Van der Waals dimers we have calculated the harmonic frequencies of the Van der Waals vibrations, as described in Section 3. The results shown in Table 1 indicate that in all dimers the geared internal rotations are relatively soft and the anti-gearied rotations are considerably stiffer. The torsional frequencies are intermediate between these extremes. The Van der Waals stretch mode has typical frequencies of 30 to 50 cm$^{-1}$, substantially higher than the 11 to 13 cm$^{-1}$ estimated in Ref. 7 for $(SF_6)_2$. 

Fig. 1 Equilibrium structures of the dimers calculated with the atom-atom potential.
Table 1. Van der Waals vibrations (harmonic)

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$A$</th>
<th>$B$</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geared rotation</td>
<td>5.4</td>
<td>$0.6R_x - 0.8R_y - 0.8R_z + 0.6R_y$</td>
<td>$-0.8R_x + 0.6R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>5.4</td>
<td>$0.6R_x + 0.8R_y - 0.8R_z - 0.6R_y$</td>
<td>$-R_x$</td>
<td>$B_1$ ($D_{ac}$)</td>
</tr>
<tr>
<td>Torsion</td>
<td>21.9</td>
<td>$R_x$</td>
<td>$-R_x$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Stretch</td>
<td>30.5</td>
<td>$x$</td>
<td>$-z$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>38.2</td>
<td>$0.8R_x - 0.8R_y$</td>
<td>$0.6R_z - 0.8R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Stretch</td>
<td>30.5</td>
<td>$x$</td>
<td>$-z$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>38.2</td>
<td>$0.8R_x + 0.8R_y$</td>
<td>$0.6R_z + 0.8R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Geared rotation</td>
<td>7.7</td>
<td>$R_x$</td>
<td>$-R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>7.7</td>
<td>$R_x$</td>
<td>$-R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Torsion</td>
<td>49.0</td>
<td>$R_x$</td>
<td>$-R_x$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Stretch</td>
<td>60.2</td>
<td>$R_x$</td>
<td>$R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>60.2</td>
<td>$R_x$</td>
<td>$R_y$</td>
<td>$E$</td>
</tr>
<tr>
<td>Geared rotation</td>
<td>16.3</td>
<td>$R_x$</td>
<td>$-R_y$</td>
<td>$B_2$</td>
</tr>
<tr>
<td>Geared rotation</td>
<td>27.4</td>
<td>$R_x$</td>
<td>$-R_y$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>Stretch</td>
<td>35.0</td>
<td>$z$</td>
<td>$-z$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>Torsion</td>
<td>36.3</td>
<td>$R_x$</td>
<td>$-R_y$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>50.6</td>
<td>$R_x$</td>
<td>$R_y$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>Antigeared rotation</td>
<td>112.0</td>
<td>$R_x$</td>
<td>$R_y$</td>
<td>$B_2$</td>
</tr>
</tbody>
</table>

A further exploration of the potential energy surface was made by calculating the barriers to internal rotation along the paths indicated by the Van der Waals normal modes. It is confirmed by these calculations that the geared internal rotations are much easier than the anti-geared ones. Still, in $(\text{SF}_6)_2$ and $(\text{SiF}_4)_2$ the rotational barriers associated with the geared rotations are higher than 125 cm$^{-1}$. In $(\text{SiH}_4)_2$, however, the barriers for the geared internal rotations are only 17 cm$^{-1}$, when the distance $R$ is relaxed. This value is comparable with the zero-point energy for the geared rotation-vibrations, see Table 1. So we can expect large amplitude hindered rotations for this degree of freedom in $(\text{SiH}_4)_2$. Another mode which seems relatively soft and has a low barrier to rotation is the torsional mode in $(\text{SiF}_4)_2$, but this depends specifically on the calculated equilibrium structure. At the experimental molecular beam temperatures of about 20 K several Van der Waals vibrational states will be populated in all the dimers considered (cf. the frequencies in Table 1). Most of the orientational modes, especially in $(\text{SF}_6)_2$ and $(\text{SiF}_4)_2$, are "locked"; the Van der Waals vibrations will be librations about the equilibrium angles. For the geared internal rotations in $(\text{SiH}_4)_2$ they will be hindered rotations with large amplitudes, just below and above the rotation barriers. The amplitudes for the rotational vibrations in the latter dimer will be larger anyway, because of the large rotational constant of $\text{SiH}_4$. This contradicts the lesser orientational mobility assumed for $(\text{SiH}_4)_2$ in Ref. 4. The interpretation of the photodissociation spectra of these dimers will have to be consistent with this picture.
Next we have calculated the frequencies and the intensities of the dimer vibrational transitions in the range of the $\nu_3$ vibrations of SF$_6$ and SiF$_4$ and the $\nu_4$ vibration of SiH$_4$. The force fields used for the monomers are given in Ref. 8. We have analyzed the various contributions to the splitting and shifts of the monomer frequencies, and we have investigated the orientational dependence of each contribution, as well as the orientational dependence of the dimer transition strengths. From the results in Table 2 we conclude that the electrostatic contributions are dominant in all cases. As explained in Section 2, the electrostatic dipole-dipole shifts (indicated in parentheses) are $-2\Delta$, $-\Delta$, $\Delta$ and $2\Delta$, for all dimers, independent of the monomer orientations. Also the dipole-induced dipole shifts have constant ratios $-4 : -1 : -1 : -4$, independent of the monomer orientations.

In (SF$_6$)$_2$ the effects of the exchange and dispersion couplings on the dimer frequencies are completely negligible. Therefore, the (SF$_6$)$_2$ photodissociation spectrum shows the characteristic two peaks with shifts $-2\Delta$ and $\Delta$, and intensities $1 : 2$, from the excitation of the modes 1 and 4, 5 (the other excitations are forbidden in this case). In (SiF$_4$)$_2$ the exchange and dispersion effects are somewhat larger, but they are partly cancelled by the non-dipolar electrostatic and induction effects and, so, the (SiF$_4$)$_2$ spectrum still shows the characteristic two peaks, see Fig. 2. As illustrated in Fig. 2, the calculated (SiF$_4$)$_2$ spectrum is nearly independent of the monomer orientations, just as the (SF$_6$)$_2$ spectrum.

Table 2. Vibrational frequency shifts

<table>
<thead>
<tr>
<th>mode</th>
<th>electrostatic$^a$</th>
<th>exchange$^b$</th>
<th>dispersion$^c$</th>
<th>induction$^d$</th>
<th>total$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SF$_6$</td>
<td>-11.20 (-12.36)</td>
<td>0.23 (0.02)</td>
<td>-0.13 (-0.07)</td>
<td>-1.44 (-1.13)</td>
<td>-12.55 (-12.54)</td>
</tr>
<tr>
<td>2,3 SF$_6$</td>
<td>-6.44 (-6.18)</td>
<td>0.01 (0.00)</td>
<td>0.01 (0.01)</td>
<td>-0.46 (-0.28)</td>
<td>-6.89 (-6.46)</td>
</tr>
<tr>
<td>4,5 SF$_6$</td>
<td>6.20 (6.18)</td>
<td>0.00 (0.00)</td>
<td>0.02 (0.01)</td>
<td>-0.43 (-0.28)</td>
<td>5.79 (5.91)</td>
</tr>
<tr>
<td>6 SF$_6$</td>
<td>11.48 (12.36)</td>
<td>0.24 (0.06)</td>
<td>-0.12 (-0.09)</td>
<td>-1.35 (-1.13)</td>
<td>10.25 (11.21)</td>
</tr>
<tr>
<td>1 SiF$_4$</td>
<td>-8.84 (-7.81)</td>
<td>3.51 (0.08)</td>
<td>-0.79 (-0.12)</td>
<td>-1.61 (-0.65)</td>
<td>-7.74 (-7.98)</td>
</tr>
<tr>
<td>2,3 SiF$_4$</td>
<td>-3.25 (-3.05)</td>
<td>-0.09 (-0.03)</td>
<td>0.05 (0.09)</td>
<td>-0.22 (-0.16)</td>
<td>-3.51 (-3.81)</td>
</tr>
<tr>
<td>4,5 SiF$_4$</td>
<td>3.35 (3.65)</td>
<td>-0.11 (0.00)</td>
<td>0.05 (0.01)</td>
<td>-0.23 (-0.16)</td>
<td>3.06 (3.51)</td>
</tr>
<tr>
<td>6 SiF$_4$</td>
<td>7.29 (7.31)</td>
<td>0.05 (0.31)</td>
<td>-0.28 (-0.19)</td>
<td>-0.79 (-0.63)</td>
<td>7.15 (7.79)</td>
</tr>
<tr>
<td>1 SiH$_4$</td>
<td>-5.10 (-5.51)</td>
<td>1.50 (0.27)</td>
<td>-0.82 (-0.40)</td>
<td>-0.91 (-0.49)</td>
<td>-5.33 (-6.13)</td>
</tr>
<tr>
<td>2 SiH$_4$</td>
<td>-3.06 (-2.76)</td>
<td>-0.66 (0.04)</td>
<td>0.37 (-0.04)</td>
<td>-0.26 (-0.12)</td>
<td>-3.61 (-2.88)</td>
</tr>
<tr>
<td>3 SiH$_4$</td>
<td>-0.82 (-2.76)</td>
<td>1.74 (-0.02)</td>
<td>-0.78 (0.08)</td>
<td>-0.66 (-0.12)</td>
<td>-2.62 (2.62)</td>
</tr>
<tr>
<td>4 SiH$_4$</td>
<td>0.32 (2.76)</td>
<td>1.01 (0.04)</td>
<td>-0.36 (-0.04)</td>
<td>-0.27 (-0.12)</td>
<td>0.70 (2.63)</td>
</tr>
<tr>
<td>5 SiH$_4$</td>
<td>3.92 (2.76)</td>
<td>-0.36 (-0.02)</td>
<td>0.25 (0.07)</td>
<td>-0.22 (-0.12)</td>
<td>3.59 (2.68)</td>
</tr>
<tr>
<td>6 SiH$_4$</td>
<td>6.72 (5.51)</td>
<td>4.60 (0.27)</td>
<td>-1.58 (-0.45)</td>
<td>-0.64 (-0.49)</td>
<td>9.11 (4.84)</td>
</tr>
</tbody>
</table>

$^a$ In cm$^{-1}$, calculated for the dimer equilibrium structures.

$^b$ The numbers in parentheses are the leading terms in the expansion about the molecular centers of mass; for the electrostatic contribution this is the resonant dipole-dipole splitting, for the induction contribution this is the dipole-induced dipole shift.

$^c$ These modes are degenerate.
For (SiH$_4$)$_2$ the situation is markedly different. Here, we find (see Table 2) that the vibrational frequency splitting and shifts caused by the exchange and dispersion interactions are not negligible. Still, they are dominated by the electrostatic effects. It is most remarkable, however, that the electrostatic coupling terms in this case do not lead to the usual two peaks with the familiar 1:2 intensity relation. A more irregular pattern is obtained, both for the peak positions and their intensities, which, moreover, depends strongly on the monomer orientations. For the two directions of easy (geared) rotation in (SiH$_4$)$_2$ this is illustrated in Fig. 3. The effect of the relaxation of the distance $R$, which accompanies the geared rotations, is included in Fig. 3. This effect is very small, however, in comparison with the changes in the spectrum that are caused directly by the monomer rotations. From an analysis of the calculated results which have yielded Fig. 3 we conclude that in (SiH$_4$)$_2$ not only the leading (dipole-dipole) term in the multipole expansion of the electrostatic coupling $V_{HH}^{(2)}$ is important, but also the higher terms. These higher terms lead to resonance effects between the monomer vibrations in (SiH$_4$)$_2$ which are orientationally dependent. The mixing of the monomer excitations is more complicated than given by Eq. (9), which is reflected by the frequencies of the dimer vibrations, as well as by their intensities. Excitations of all dimer modes become allowed, in this case.

Given this conclusion we can at least understand why the photodissociation spectrum of (SiH$_4$)$_2$ is qualitatively different from the spectra of (SF$_6$)$_2$ and (SiF$_4$)$_2$. For all these complexes, several Van der Waals vibrational states will be populated at the experimental beam temperatures. The structure of the vibrational spectra in the range from 880 to 1100 cm$^{-1}$ must be explained by summation of the spectra of all these Van der Waals states. Together with the effects from Coriolis couplings, this will lead to inhomogeneous line broadening, because of the variations in the average intermolecular bond length $\langle R \rangle$ for the different Van der Waals vibrational states. In all dimers we have orientational vibrations also, but this will only lead to additional broadening (and shifting) of the lines when the line positions depend on the monomer orientations.
This occurs for \((\text{SiH}_4)_2\) only, cf. Figs. 2 and 3, and it is more important than the line shifts caused by the variations of \(\langle R \rangle\). Moreover, the amplitudes of the orientational vibrations, especially of the geared modes, are larger in \((\text{SiH}_4)_2\). Although we may expect that the origin of the qualitatively different \((\text{SiH}_4)_2\) spectrum is related to these effects, we cannot yet reproduce the experimental spectrum from our calculations. We would need to calculate explicitly the large amplitude Van der Waals vibrational states and to take a thermal average over those states. This would be an enormous task which is not practically possible without drastic approximations. The intermolecular model potential is not sufficiently accurate to justify such an effort. Moreover, it would be preferable to first obtain more detailed experimental information on the \((\text{SiH}_4)_2\) spectrum. In particular, it would be very informative to study \((\text{SiH}_4)_2\) by the same double-resonance techniques that have been applied to \((\text{SF}_8)_2\) and \((\text{SiF}_4)_2\). For the latter dimers these techniques have confirmed the resonant dipole-dipole mechanism of the vibrational coupling; for \((\text{SiH}_4)_2\) they will yield new information that verifies the effects found in our model calculations.

We have checked whether our conclusions do not depend specifically on the parameters chosen for the atom-atom potential. We have replaced the values for the F-parameters in \((\text{SiF}_4)_2\) and the values for the H-parameters in \((\text{SiH}_4)_2\) by values from another reference (see Ref. 8). Although this leads to somewhat different equilibrium structures of the dimers and, therefore, slightly different sizes of the vibrational frequency shifts, it does not change the overall conclusions. The size of our calculated splitting is not accurate, anyway, because we have used the values of \(R_0\) calculated with the atom-atom potential, rather than extracted \(R_0\) from the spectra as in Ref. 4.
Finally, we have addressed the question why the higher (orientationally dependent) electrostatic resonance couplings are important in \((\text{SiH}_4)_2\) but not in \((\text{SiF}_4)_2\) and \((\text{SF}_6)_2\). The ratio between the intramolecular bond length \(r_i^{(0)}\) and the Van der Waals bond length \(R_\text{v}\), which determines the convergence of the molecular multipole expansion of the couplings, is practically the same for all dimers. However, the amplitude of vibration of the light H-atoms in \(\text{SiH}_4\) is much larger than the amplitude of the F-atoms in \(\text{SiF}_4\) and \(\text{SF}_6\), in both the \(\nu_3\) and \(\nu_4\) modes. Through the transformation of the coupling matrices to monomer normal coordinates \(Q_A\) and \(Q_B\), see Eqs. (5) to (7), this enters the calculated shifts of the vibrational frequencies in the dimers, see Eq. (8). So, the contribution of the ligand displacements to these shifts is much larger in \((\text{SiH}_4)_2\) than in \((\text{SF}_6)_2\) and \((\text{SiF}_4)_2\) and, therefore, the orientationally dependent (higher) coupling terms are considerably more important.

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REFERENCES

8. J.W.I. van Bladel and A. van der Avoird, to be published.