

Structure and frequency shift calculations for small UF₆ clusters

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Abstract

A new site–site intermolecular potential for UF₆, featuring exchange, dispersion, electrostatic and induction terms, is presented. The new potential is used to determine UF₆ cluster structures up to the hexamer and, by means of a second order line shift formalism, to calculate the corresponding IR spectra in the region of the ν_3 vibrational mode. © 1997 Elsevier Science B.V.

Keywords: Cluster; Structure; Perturbation; Lineshift; SF₆; UF₆

1. Introduction

Through the frequency shift in the IR absorption of the UF₆ monomer, the UF₆ cluster formation is considered to adversely affect the selectivity in the molecular laser isotope separation with the supersonic expansion technique.

Recently we have reported a new site–site intermolecular potential for the less demanding SF₆ system [1], the structures obtained for clusters up to the hexamer, and the corresponding frequency shifts of the ν_3 vibrational monomer mode. Basically, we follow the same pattern for establishing the site–site intermolecular potential of UF₆, by fitting it to the observed temperature dependence of the second virial coefficient. The adjusted UF₆–UF₆ potential is used to determine UF₆ cluster structures up to the hexamer, for which the IR spectrum in the region of the ν_3 mode (at 627.724 cm⁻¹) is calculated.

2. Intermolecular potential models

The functional form of the intermolecular potential we have chosen for calculating the structures of the UF₆ clusters, and the corresponding vibrational frequencies shifts comprises exchange, dispersion, electrostatic, and induction terms:

$$U^{\text{exch}} = \sum_{m=1}^{M-1} \sum_{m'=m+1}^M \sum_{i \in m} \sum_{j \in m'} A_{ij} \exp(-B_{ij} r_{ij})$$

$$U^{\text{disp}} = - \sum_{m=1}^{M-1} \sum_{m'=m+1}^M \sum_{i \in m} \sum_{j \in m'} \frac{C_{ij}}{r_{ij}^6}$$

$$U^{\text{elec}} = \sum_{m=1}^{M-1} \sum_{m'=m+1}^M \sum_{i \in m} \sum_{j \in m'} \frac{q_i q_j}{r_{ij}}$$

$$U^{\text{ind}} = - \frac{1}{2} \sum_{m=1}^M \sum_{i \in m} \alpha_i \left| \sum_{m'=1}^M \sum_{j \in m'} \frac{q_j \hat{r}_{ij}}{r_{ij}^2} \right|^2$$

$m' \neq m$

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Table 1

Parameters for the intermolecular potential models of UF₆ (d_{iU} is the distance from a particular site to the U atom along the bond on which the former is located)

Potential model	Site	d_{iU} (Å)	A_{ii} (kJ mol ⁻¹)	B_{ii} (Å ⁻¹)	C_{ii} (kJ mol ⁻¹ Å ⁻⁶)	$q_i(e)$	α_i (Å ³)
Potential I	U		2 560 200	2.642	89 850	6	
	F	1.9962	336 133	4.128	665.9	0	
	e ⁻	1.3500	0	0	0	-1	
Potential II	U		2 560 200	2.642	89 850	6	7.9338
	F	1.9962	336 133	4.128	665.9	0	0.7557
	e ⁻	1.3500	0	0	0	-1	0

where r_{ij} is the distance between atom i belonging to monomer m and atom j belonging to monomer m' , q_i are the effective charges placed on the atoms, and α_i is the polarizability of site i . Additional "electronic" sites have been defined on the U–F bonds, which are supposed to account for the six valence electrons of uranium (5f³6d¹ 7s²).

We employ two variants of the above potential model: the first one, designated as "potential I", does not include the induction term, while the second, denoted as "potential II", includes all the interactions.

In order to make our potential models as realistic as possible, we have adjusted their parameters in accordance with two macroscopic aspects: the transition dipole moment of the monomer and the temperature dependence of the second virial coefficient. As a reference for determining the effective charges q_i placed on the sites of the UF₆ monomer, we have considered the transition dipole moment value $\mu_{01} = 0.385$ D of Kim and Person [2]. The coefficients A_{ij} , B_{ij} , and C_{ij} , defining the exchange and dispersion potentials, can be constructed from the coefficients A_{ii} , B_{ii} , and C_{ii} of the individual atomic species

by applying the standard combination rules. For fluorine, we have considered the previously determined values [1]. As for uranium, due to the lack of any reliable U–U potential in the literature, we have resorted to fitting the coefficients with respect to the temperature dependence of the second virial coefficient of UF₆.

All relevant data for the description of our potential models are summarized in Table 1.

3. Cluster structures

In order to calculate the cluster structures, we consider the molecules "frozen" in their equilibrium geometries and minimize the intermolecular potential with respect to their relative positions starting from randomly chosen initial configurations.

The results of our cluster structure calculations are summarized in Table 2. The mean U–U bond length are an indication of the "compactness" of the clusters. For all cluster sizes we have listed the data for the most stable isomer. The geometrical configurations of the clusters showing symmetry properties

Table 2

Calculated UF₆ cluster structures for the most stable isomers

M	Potential I		Potential II		Symmetry
	E	d_{UU}	E	d_{UU}	
2	-8.66	5.381	-8.72	5.375	D_{2d}
3	-23.46	5.487	-23.74	5.477	D_3
4	-40.77	5.672	-41.20	5.666	C_3
5	-62.99	5.674	-63.41	5.669	C_{3h}
6	-86.17	5.741	-86.66	5.738	

E represents the total binding energy (in kJ mol⁻¹), and d_{UU} is the average U–U distance (in Å).

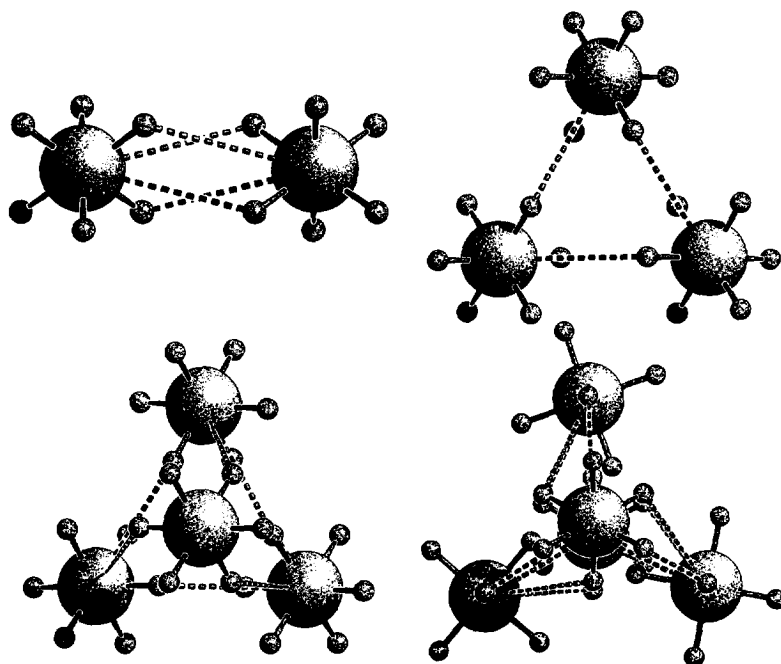


Fig. 1. Geometrical structures of the symmetrical UF₆ clusters (dimer, trimer, tetramer, and pentamer).

are presented in Fig. 1. It should be noted that the cluster structures are alike for both potential models.

4. Frequency shifts

In our band shift calculations we have focused on the fundamental excitation of the ν_3 vibrational mode (at 627.724 cm^{-1}). For the evaluation of the intermolecular potential derivatives with respect to the vibrational coordinates occurring in the frequency shift expressions, the so-called \tilde{I} -matrix is needed [1], which results as part of the normal mode analysis of the monomer, performed according to the G-F method of Wilson [4]. We have employed the U–F bond length of 1.9962 \AA and the quadratic intramolecular force field reported by Aldridge et al. [3]. The transformation of the force constants from symmetry to normal coordinates, yielding the cubic force constants ϕ_{rst} which enter the expressions of the second order line shifts, is performed by the L -tensor method of Hoy et al. [5].

The individual contributions of the various potential terms to the line shifts have been evaluated, and it

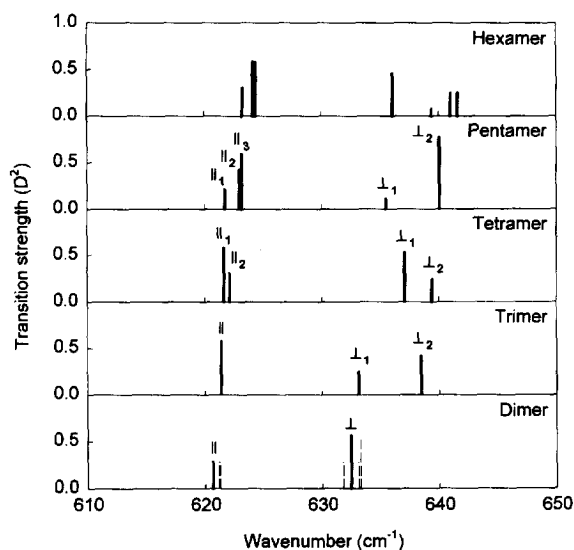


Fig. 2. Calculated stick spectra of UF₆ clusters from dimer to hexamer using potential I. The spectral lines for the second and third lowest dimer are plotted with dotted line.

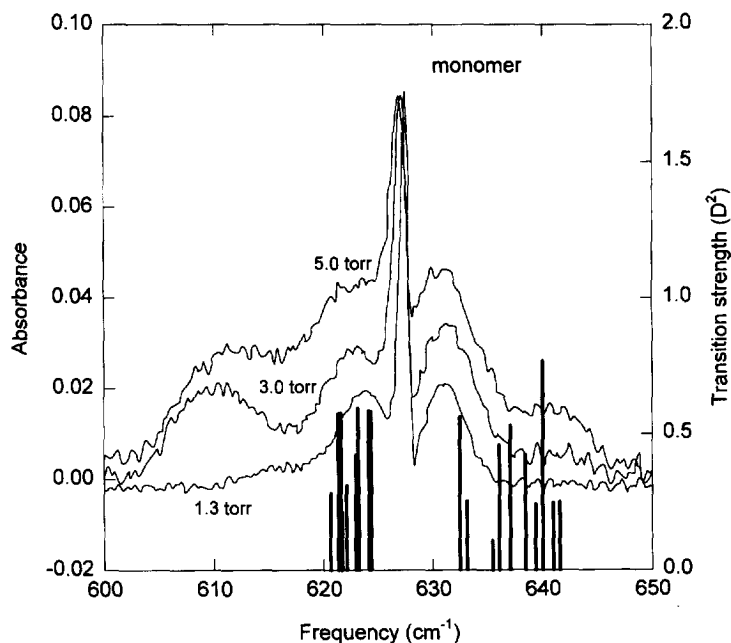


Fig. 3. FTIR spectra of UF_6 clusters (Ref. [6]) and calculated stick spectra by using potential I.

turns out that, through the vibrational dipole–dipole interaction, the electrostatic contributions are dominant.

Fig. 2 shows the stick spectra of the UF_6 clusters up to the hexamer, obtained by using potential I.

The only available experimental data about the UF_6 clusters are the recent FTIR spectroscopy measurements of Tanimura et al. [6]. Fig. 3 shows the FTIR spectra of the ν_3 band of UF_6 seeded in Ar at a mole fraction of 0.08 mol mol⁻¹ and total pressures equal to 1.3, 3.0, and 5.0 Torr, along with the stick spectra obtained with potential I. Whereas the peaks at 623 and 632 cm⁻¹ also contain contributions from the P and R branches of the monomer spectrum, the peak at 640 cm⁻¹ is clearly due to the presence of the UF_6 clusters solely, because it does not practically appear in the spectrum at 1.3 Torr. Since our calculations do not evidence dimer lines around 640 cm⁻¹, it follows that this peak should be attributed to the higher clusters, which are consequently formed only above 3.0 Torr. In the blue shifted band around 632 cm⁻¹

there are only contributions from the dimer and the trimer, while in the red shifted band around 623 cm⁻¹, there are contributions from all cluster sizes. We did not find any theoretical line corresponding to the peak around 610 cm⁻¹ appearing in the FTIR spectrum at 3.0 Torr, which could be possibly due to mixed UF_6 –Ar clusters.

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