Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Rovibrational laser jet-cooled spectroscopy of SF_6-rare gas complexes in the ν_3 region of SF_6

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Supplementary Material

Content:

Fig.S1 EC-QCL jet cooled spectra of the ν_3 band of SF_6 monomer for 0.12 % SF_6 (bottom), and for 0.12% SF_6 and 1% Ar (middle) diluted in 8 bar helium at an axial distance z = 15 mm for the pin hole nozzle. The spectrum of SF_6-Ar obtained after subtraction of both jet-cooled spectra is displayed above.

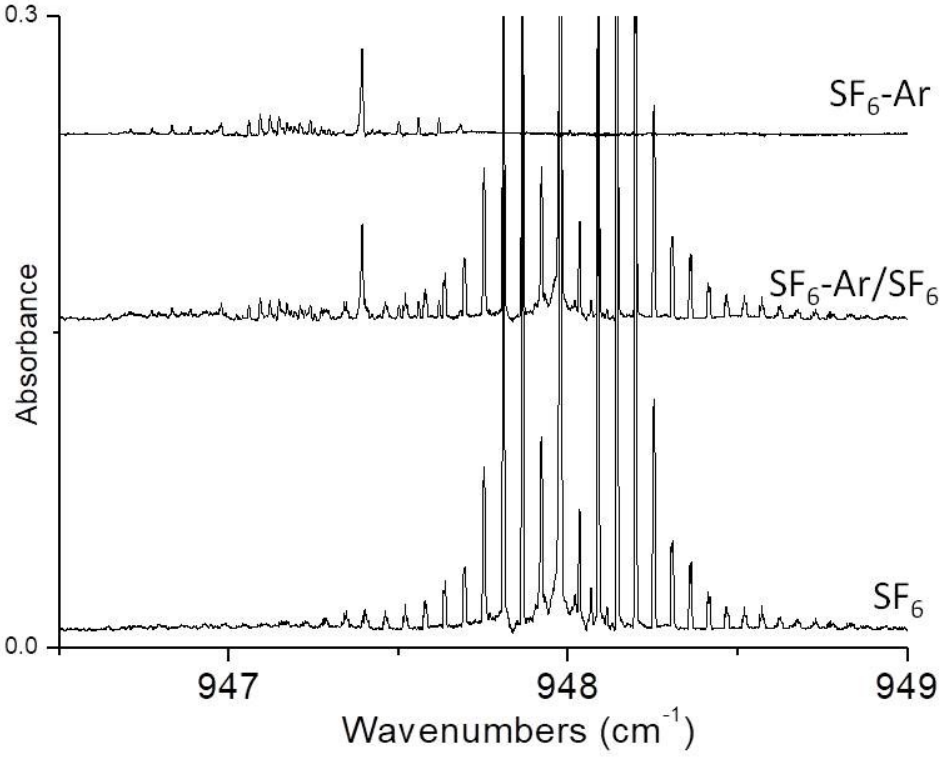

Table S1 : List of transitions frequencies of SF_6-Rg (Rg = Ar, Kr, Xe) hetero dimers assigned and used to simulate the rovibrational parallel and perpendicular band contours.

SF_6-Ar parallel band

Calc. Frequency	J’	K’	l’	J’’	K’’
946.97677	1	1		1	1
946.97151	2	2		2	2
946.96186	3	2		3	2
946.96186	4	4		4	4
946.95479	3	1		3	1
946.94504	4	2		4	2
946.93612	0	0		1	0
946.88632	1	0		2	0
946.88632	1	1		2	1
946.83171	2	0		3	0
946.83171	2	1		3	1
946.77305	3	0		4	0
946.77305	3	1		4	1
946.71005	4	0		5	0
946.71005	4	1		5	1
946.64723	5	0		6	0
946.64723	5	1		6	1
947.02187	1	0		0	0
947.05905	2	0		1	0
947.05905	2	1		1	1
947.09159	3	0		2	0
947.09159	3	1		2	1
947.12056	4	0		3	0
947.12056	4	1		3	1
947.14713	5	0		4	0
947.14713	5	1		4	1
947.17081	6	0		5	0
947.17081	6	1		5	1
947.17081	6	2		5	2
947.18282	7	0		6	0
947.18282	7	1		6	1
946.97677	1	1		1	1
946.97151	2	2		2	2
946.96186	3	2		3	2
946.96186	4	4		4	4
946.95479	3	1		3	1
946.94504	4	2		4	2
946.93612	0	0		1	0
946.88632	1	0		2	0
946.88632	1	1		2	1
946.83171	2	0		3	0

946.83171	2	1	3	1
946.77305	3	0	4	0
946.77305	3	1	4	1
946.71005	4	0	5	0
946.71005	4	1	5	1
946.64723	5	0	6	0
946.64723	5	1	6	1
947.02187	1	0	0	0
947.05905	2	0	1	0
947.05905	2	1	1	1
947.09159	3	0	2	0
947.09159	3	1	2	1
947.12056	4	0	3	0
947.12056	4	1	3	1
947.14713	5	0	4	0
947.14713	5	1	4	1
947.17081	6	0	5	0
947.17081	6	1	5	1
947.17081	6	2	5	2
947.18282	7	0	6	0
947.18282	7	1	6	1
946.97677	1	1	1	1
946.97151	2	2	2	2
946.96186	3	2	3	2
946.96186	4	4	4	4
946.95479	3	1	3	1
946.94504	4	2	4	2
946.93612	0	0	1	0
946.88632	1	0	2	0
946.88632	1	1	2	1
946.83171	2	0	3	0

SF_6-Kr Parallel band

946.45264	5	0	6	0
946.4529	5	1	6	1
946.45368	5	2	6	2
946.45498	5	3	6	3
946.4568	5	4	6	4
946.4875	4	0	5	0
946.48776	4	1	5	1
946.48854	4	2	5	2
946.48984	4	3	5	3
946.49166	4	4	5	4
946.52104	3	0	4	0
946.5213	3	1	4	1
946.52208	3	2	4	2
946.52338	3	3	4	3
946.55326	2	0	3	0
946.55352	2	1	3	1
946.5543	2	2	3	2

946.58416	1	0	2	0
946.58442	1	1	2	1
946.617	9	9	9	9
946.617	9	8	9	8
946.617	9	7	9	7
946.617	9	6	9	6
946.617	9	5	9	5
946.617	9	4	9	4
946.617	9	3	9	3
946.6186	0	0	1	0
946.66894	1	0	0	0
946.66894	1	0	0	0
946.741334	4	0	3	0
946.74134	4	1	3	1
946.741358	4	2	3	2
946.741387	4	3	3	3
946.7635	5	0	4	0
946.76376	5	1	4	1
946.76454	5	2	4	2
946.76584	5	3	4	3
946.76766	5	4	4	4
946.78384	6	0	5	0
946.7841	6	1	5	1
946.78488	6	2	5	2
946.78618	6	3	5	3
946.788	6	4	5	4
946.80286	7	0	6	0
946.80312	7	1	6	1
946.8039	7	2	6	2
946.8052	7	3	6	3
946.80702	7	4	6	4
946.45264	5	0	6	0
946.4529	5	1	6	1
946.45368	5	2	6	2
946.45498	5	3	6	3
946.4568	5	4	6	4
946.4875	4	0	5	0
946.48776	4	1	5	1
946.48854	4	2	5	2
946.48984	4	3	5	3
946.49166	4	4	5	4
946.52104	3	0	4	0
946.5213	3	1	4	1
946.52208	3	2	4	2
946.52338	3	3	4	3
946.55326	2	0	3	0
946.55352	2	1	3	1
946.5543	2	2	3	2
946.58416	1	0	2	0
946.58442	1	1	2	1
946.617	9	9	9	9
946.617	9	8	9	8

946.617	9	7		9	7
946.617	9	6		9	6
946.617	9	5		9	5
946.617	9	4		9	4
946.617	9	3		9	3
946.6186	0	0		1	0
946.66894	1	0		0	0
946.66894	1	0		0	0
946.741334	4	0		3	0
946.74134	4	1		3	1
946.741358	4	2		3	2
946.741387	4	3		3	3
946.7635	5	0		4	0
946.76376	5	1		4	1
946.76454	5	2		4	2
946.76584	5	3		4	3
946.76766	5	4		4	4
946.78384	6	0		5	0
946.7841	6	1		5	1
946.78488	6	2		5	2
946.78618	6	3		5	3
946.788	6	4		5	4
946.80286	7	0		6	0
946.80312	7	1		6	1
946.8039	7	2		6	2
946.8052	7	3		6	3
946.80702	7	4		6	4

SF_6-Kr Perpendicular band

947.009916	2	2	-1	3	3
947.035404	2	1	-1	3	2
947.036555	4	1	1	5	0
947.063200	1	1	-1	2	2
947.063931	3	1	1	4	0
947.064270	2	0	--	3	1
947.091527	2	1	1	3	0
947.092086	1	0	--	2	1
947.096892	1	0	--	1	1
947.097180	2	0	--	2	1
947.097612	3	0	--	3	1
947.098188	4	0	--	4	1
947.098908	5	0	--	5	1
947.099772	6	0	--	6	1
947.122484	1	1	1	1	0
947.122772	2	1	1	2	0
947.123204	3	1	1	3	0
947.123780	4	1	1	4	0
947.124500	5	1	1	5	0
947.125364	6	1	1	6	0
947.126372	7	1	1	7	0

947.150212	1	1	1	0	0
947.151220	2	2	1	2	1
947.151652	3	2	1	3	1
947.152228	4	2	1	4	1
947.152948	5	2	1	5	1
947.153812	6	2	1	6	1
947.178935	5	1	1	5	0
947.179284	2	1	1	1	0
947.206964	3	1	1	2	0
947.207732	2	2	1	1	1
947.251804	3	3	1	2	2
947.288644	3	2	1	2	1
947.288756	4	1	1	3	0
947.314492	4	2	1	3	1
947.316940	5	1	1	4	0
947.342876	4	3	1	3	2
947.343468	5	2	1	4	1
947.346060	6	1	1	5	0
947.365316	4	4	1	3	3
947.365652	5	3	1	4	2
947.373116	4	4	1	3	3

SF_6-Xe Parallel band

945.99058	9	0		10	0
945.99058	9	1		10	1
945.99058	9	2		10	2
946.01614	8	0		9	0
946.01614	8	1		9	1
946.01614	8	2		9	2
946.04168	7	0		8	0
946.04168	7	1		8	1
946.04168	7	2		8	2
946.06614	6	0		7	0
946.06614	6	1		7	1
946.09048	5	0		6	0
946.09048	5	1		6	1
946.09048	5	2		6	2
946.11415	4	0		5	0
946.11415	4	1		5	1
946.11415	4	2		5	2
946.13765	3	0		4	0
946.13765	3	1		4	1
946.13765	3	2		4	2
946.15996	2	0		3	0
946.15996	2	1		3	1
946.15996	2	2		3	2
946.18238	1	0		2	0
946.20251	0	0		1	0
946.22112	2	2		2	2
946.22112	1	1		1	1

946.22112	3	3		3	3
946.22112	3	2		3	2
946.22112	4	3		4	3
946.22112	2	1		2	1
946.24492	1	0		0	0
946.26361	2	0		1	0
946.26361	2	1		1	1
946.28244	3	0		2	0
946.28244	3	1		2	1
946.28244	3	2		2	2
946.30083	4	0		3	0
946.30083	4	1		3	1
946.30083	4	2		3	2
946.31871	5	0		4	0
946.31871	5	1		4	1
946.31871	5	2		4	2
946.35292	7	0		6	0
946.35292	7	1		6	1
946.35292	7	2		6	2
946.36902	8	0		7	0
946.36902	8	1		7	1
946.36902	8	2		7	2
946.38455	9	0		8	0
946.38455	9	1		8	1
946.38455	9	2		8	2
946.39988	0	0		9	0
946.39988	0	1		9	1
946.39988	0	2		9	2

SF_6-Xe Perpendicular band

946.8655	4	0		4	1
946.8655	5	0		5	1
946.8655	3	0		3	1
946.8655	6	0		6	1
946.8655	7	0		7	1
946.8655	2	0		2	1
946.8655	8	0		8	1
946.8655	1	0		1	1
946.89644	4	1	1	4	0
946.89644	5	1	1	5	0
946.89644	3	1	1	3	0
946.89644	6	1	1	6	0
946.89644	2	1	1	2	0
946.89644	1	1	1	1	0
946.91795	1	1	1	0	0
946.936	5	2	1	5	1
946.936	4	2	1	4	1
946.936	6	2	1	6	1
946.936	3	2	1	3	1
946.936	7	2	1	7	1

946.936	8	2	1	8	1
946.936	2	2	1	2	1
946.936	9	2	1	9	1
946.963	3	1	1	2	0
946.9725	5	3	1	5	2
946.9725	6	3	1	6	2
946.9725	4	3	1	4	2
946.9725	7	3	1	7	2
946.9725	8	3	1	8	2
946.9725	3	3	1	3	2
946.9725	9	3	1	9	2
946.99487	3	2	1	2	1

Annex : Molecular parameters used in the fitting procedure of the SF_6-Rg experimental data with a radial one-dimensional Buckingham-type intermolecular potential

The repulsive β parameter can be estimated from the tail of the wavefunctions of the interacting molecules. From quantum defect theory,[1] the asymptotic form of the wavefunction depends upon the ionization energy of the molecule and takes the form

$$\Psi \ \alpha \ e^{-R/a_0 n_{eff}} \quad (1)$$

where a_0 is the Bohr radius and n_{eff} is an effective principal quantum number such that $n_{eff}^2 = R_d/E_i$ (R_d Rydberg constant, E_i ionization energy). By analogy with the asymptotic form of the repulsion, it comes

$$\beta = (1/n_{eff,SF_6} + 1/n_{eff,Rg})/a_0 \quad (2)$$

The values of β for SF_6-Rg obtained with Eq.(2) are derived from effective principle quantum numbers calculated from ionization potential values[2] and are reported in Table S2. C_6^{AB} coefficients for AB heterodimers are extracted from the literature using the combining rule $C_6^{AB} \approx (C_6^{AA} C_6^{BB})^{1/2}$ expected to be a good approximation.[3] The C_6^{Rg-Rg} and $C_6^{SF_6-SF_6}$ calculated coefficients are taken from recognized works of Tao et al.[4], Vydrov et al.[5] and Kumar et al.[6] and are gathered in Table S3.

Table S4 contains all the parameters required to plot the graph $\Delta\nu_{exp}(R_m^6/C_6)$ as a function of $(3\beta/R_m)$. Experimental well depths ε of the SF_6-Rg heterodimers are also derived from these parameters.

	E_i (eV)	$1/n_{eff}$		β(Å^{-1})
SF_6	15.7	1.0744		
Ne	21.565	1.2590	SF_6-Ne	4.411
Ar	15.760	1.0760	SF_6-Ar	4.065
Kr	14.000	1.0414	SF_6-Kr	3.949
Xe	12.130	0.9442	SF_6-Xe	3.816

Table S2: Ionization potential and effective principle quantum number for rare gases and SF_6 for calculating model repulsive forces and repulsive β parameters related to SF_6-Rg heterodimers.

	C_6^{Rg-Rg} *calculated*				$C_6^{SF_6-Rg}$ *From combination rules (CR)*			$C_6^{SF_6-Rg}$ *CR (mean)*
	Tao	Vydrov	Kumar		Tao	Vydrov	Kumar	
Ne-Ne	7.33	6.35	6.38	SF_6-Ne	65.5	61.0	61.1	63.3(6)
Ar-Ar	67.7	64.42	64.30	SF_6-Ar	199.1	194.3	194.1	196.7(20)
Kr-Kr	133	130.1	129.6	SF_6-Kr	279.1	276.1	275.5	277.4(27)
Xe-Xe	296	-	285.9	SF_6-Xe	416.4	416.4	409.2	412.8(41)
SF_6-SF_6	-	585.8	-					

Table S3: $C_6^{SF_6-Rg}$ coefficients (in atomic units) derived from calculated C_6^{Rg-Rg} and $C_6^{SF_6-SF_6}$ coefficients and combining rules. CR mean values are obtained by averaging sets from three distinct studies.

	$R_{e(\text{Å})}$	$\beta(\text{Å}^{-1})$	$\Delta\nu_{exp}(\text{cm}^{-1})$	$\Delta\nu_{exp}R_e^{\,6}/C_6$	$3\beta/R_e$	$\varepsilon(\text{cm}^{-1})$
SF_6-Ne	4.05(15)[a]	4.411	-0.12(3)	$-1.74\ 10^{-3}$	3.267	104
SF_6-Ar	4.302(4)[b]	4.065	-0.723(1)	$-4.84\ 10^{-3}$	2.835	227
SF_6-Kr	4.394(3)[b]	3.949	-0.981(1)	$-5.29\ 10^{-3}$	2.696	283
SF_6-Xe	4.592(1)[b]	3.816	-1.305(1)	$-6.16\ 10^{-3}$	2.493	322

(a) The SF_6-Ne bond length was roughly bracketed from both DFT-D calculations and combination rules (see text).

(b) For the complexes with heavier rare gases, experimental R_e distances were used .

Table S4: Parameters used in the model of Buckingham potential for the rare gas-SF_6 heterodimers, together with the potential depths derived from application of Formula (4) of the text.

References

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[6] A. Kumar and W. J. Meath, Mol. Phys. 54, 823 (1985).