Theoretical investigation of the spectra of rotating trimers by means of a variational quantum method based in distributed Gaussian functions

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Critical stability

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Ettore Majorana Centre for Scientific Culture

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Structure

- The DGF method.
- Vibrational spectrum.
- Geometrical structure.
- Rovibrational spectrum for J>0.

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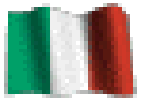
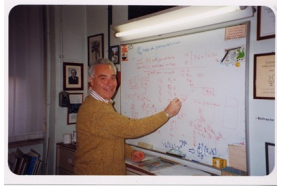


La Sapienza

Università degli Studi di Roma



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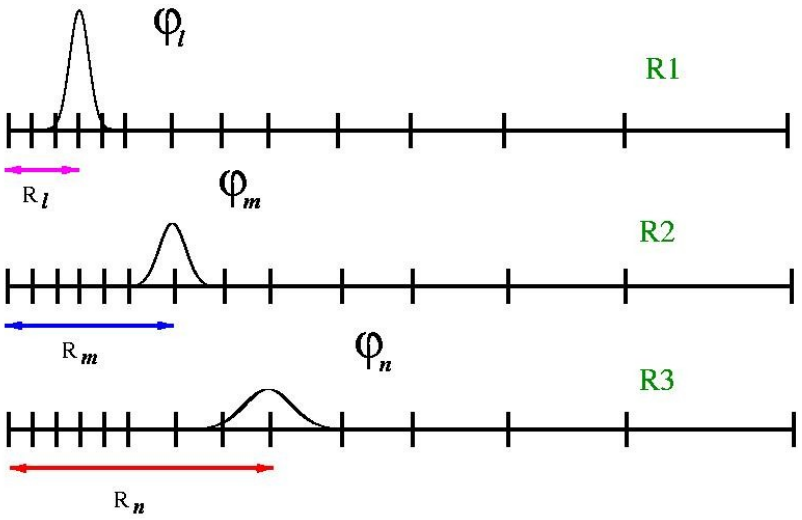
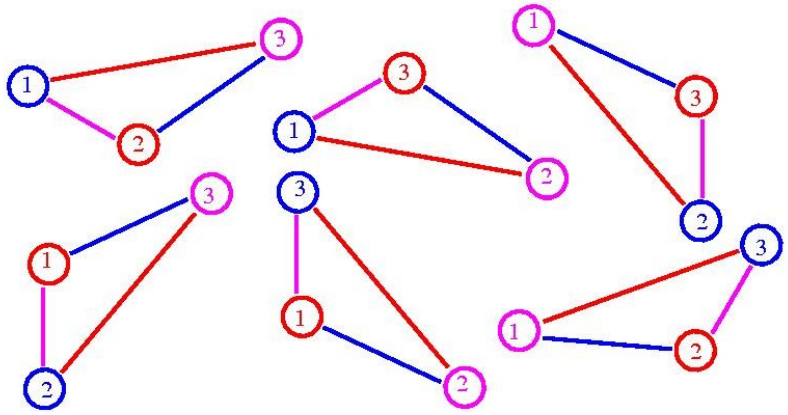
1. The DGF method

Wave function



$$\Phi_k(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3)$$

$$\phi_j = N_{lmn}^{-1/2} \sum_{P \in S_3} P[\varphi_l(R_1)\, \varphi_m(R_2)\, \varphi_n(R_3)]$$

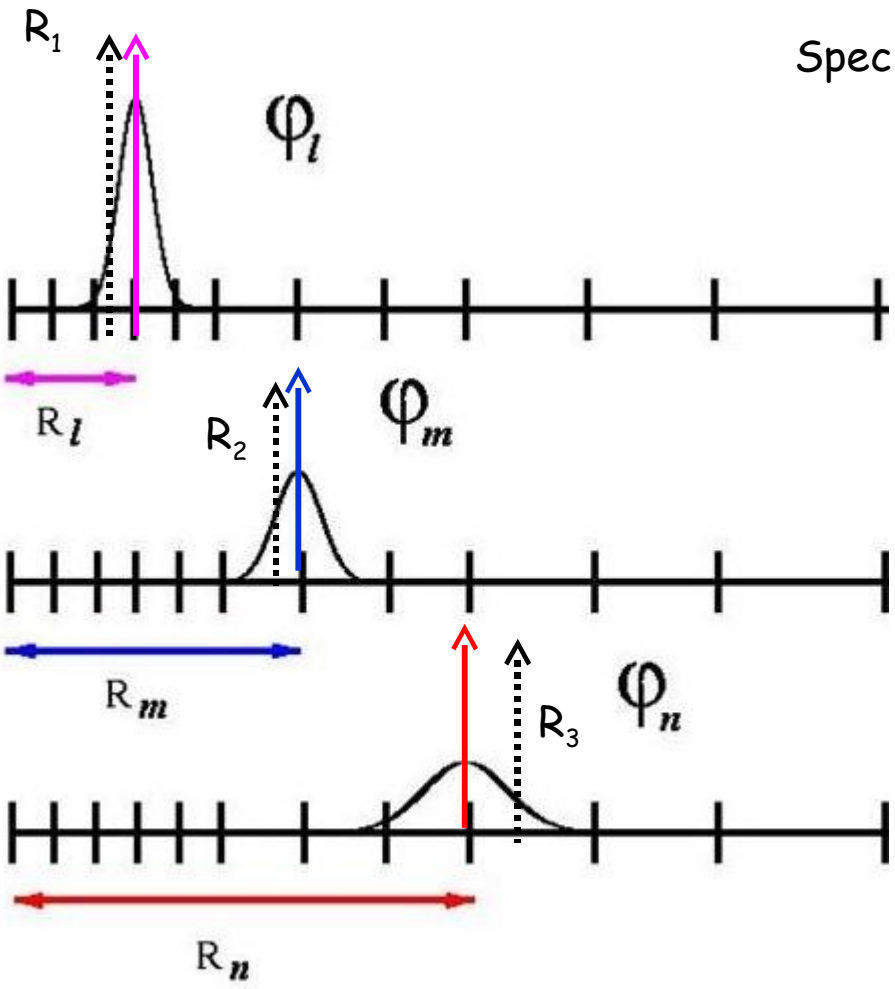


Hamiltonian

$$H = \sum_{i=1}^{3} \left\{ \frac{-\hbar^2}{m} \left[\frac{\partial^2}{\partial R_i^2} + t_i \right] + V(R_i) \right\}$$

$$t_i = \frac{1}{R_i}\frac{\partial}{\partial R_i} - \frac{1}{4R_i^2} + cos\gamma_i \left(\frac{\partial^2}{\partial R_j \partial R_k} - \frac{1}{2R_j}\frac{\partial}{\partial R_k} - \frac{1}{2R_k}\frac{\partial}{\partial R_j} + \frac{1}{4R_j R_k} \right)$$

$$cos\gamma_i = \frac{R_j^2 + R_k^2 - R_i^2}{2R_j R_k}$$



Special care for specific situations

The centers of the DGF satisfy the triangular condition:

$$|R_l - R_m| \leq R_n \leq R_l + R_m$$ ✓

Some points of the DGF might not satisfy the triangular condition:

$$|R_1 - R_2| \leq R_3 \leq R_1 + R_2$$

Definition of a badness function:

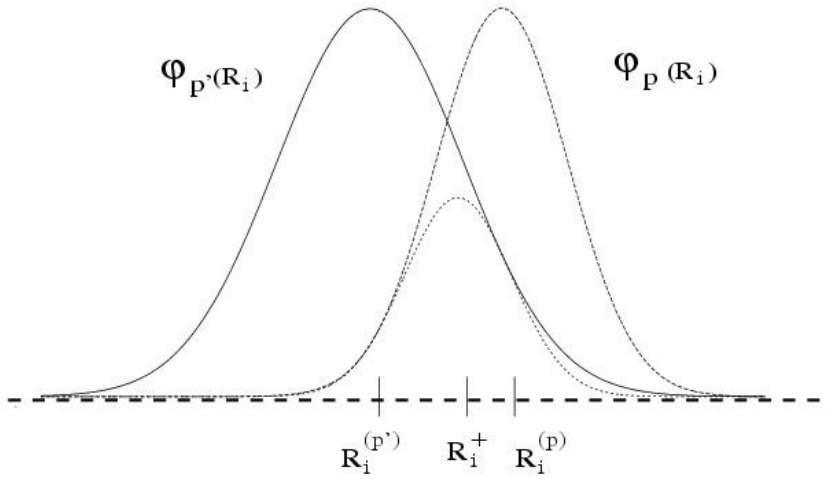
$$W(R_1,R_2,R_3)=\begin{cases}0, & |R_1-R_2|\leqslant R_3\leqslant R_1+R_2 \text{ holds}\\ 1, & \text{otherwise.}\end{cases}$$

Evaluation in terms of the DGF basis set:

$$\mathcal{I}(ll',mm',nn')\approx \tfrac{1}{2}s_{ll'}s_{mm'}s_{nn'}\{2+\mathrm{erf}[\sqrt{A_{nn'}}(|R^{\dagger}_{ll'}-R^{\dagger}_{mm'}|-R^{\dagger}_{nn'})]-\mathrm{erf}[\sqrt{A_{nn'}}(R^{\dagger}_{ll'}+R^{\dagger}_{mm'}-R^{\dagger}_{nn'})]\}.$$

$$-\mathrm{erf}[\sqrt{A_{nn'}}(|R_1-R_2|-R^{*}_{nn'})]$$

$$\sqrt{A_{nn'}}(R_1+R_2-R^{\dagger}_{nn'})]\},$$



$$s_{pp'}=\langle\varphi_p\mid\varphi_{p'}\rangle=\int dR_i\varphi_p(R_i)\varphi_{p'}(R_i),$$

$$R_i^{\dagger}=\frac{A_pR_p+A_{p'}R_{p'}}{A_p+A_{p'}}$$

	$k=2$	
E_k	$\langle\Phi_k\mid\Phi_k\rangle^{\mathrm{TIR}}$	E_k
30.25	0.9982	−28.60
30.25	0.9991	−28.42
30.25	0.9996	−28.26

2. Vibrational spectrum

Ar_3

	Morse	
k	Lanczos[d]	DGF[c]
0	−252.45	−252.45
1	−220.94	−220.94
2	−208.24	−208.24
3	−193.75	−193.74
4	−189.07	−189.06
5	−181.41	−181.40
6	−177.28	−177.27
7	−171.72	−171.72
8	−168.90	−168.90
9	−168.00	−168.00
10	−167.34	−167.33
11	−165.53	−165.48
12	−163.16	−163.04
13	−161.83	−161.68

Barrier to linearity →

c) I. Baccarelli et al. JCP **122**, 144319 (2005)

d) P. N. Roy JCP **119**, 5437 (2003)

Ne_3

	Morse	
k	Lanczos[d]	DGF[c]
0	−50.09	−50.09
1	−34.21	−34.21
2	−32.57	−32.73
3	−29.71	−29.92
4	−25.95	−26.12
5	−21.74	−21.77
6	−20.26	−20.33
7	−19.27	−19.35

Barrier to linearity →

c) I. Baccarelli et al. JCP **122**, 84313 (2005)

d) P. N. Roy JCP **119**, 5437 (2003)

Efimov states

For **3B** systems formed with **2B** systems which do not support bound states but zero energy resonances, it is possible to observe an ∞ number of bound states when $\lambda = \lambda_{2B,}$ being $V_{3B}(r) = \lambda V_{2B}(r)$.

Moreover, if λ keeps on increasing, those bound states gradually disappear.

The actual number for such Efimov states in realistic systems is given by:

$$N = \frac{1}{\pi} \ln \frac{|a|}{r_0}$$

The same eff[illegible]s found if:

- **3B** s[illegible]omean,
- Only two **2B** syst[illegible]have ZER,

For He_3, for example

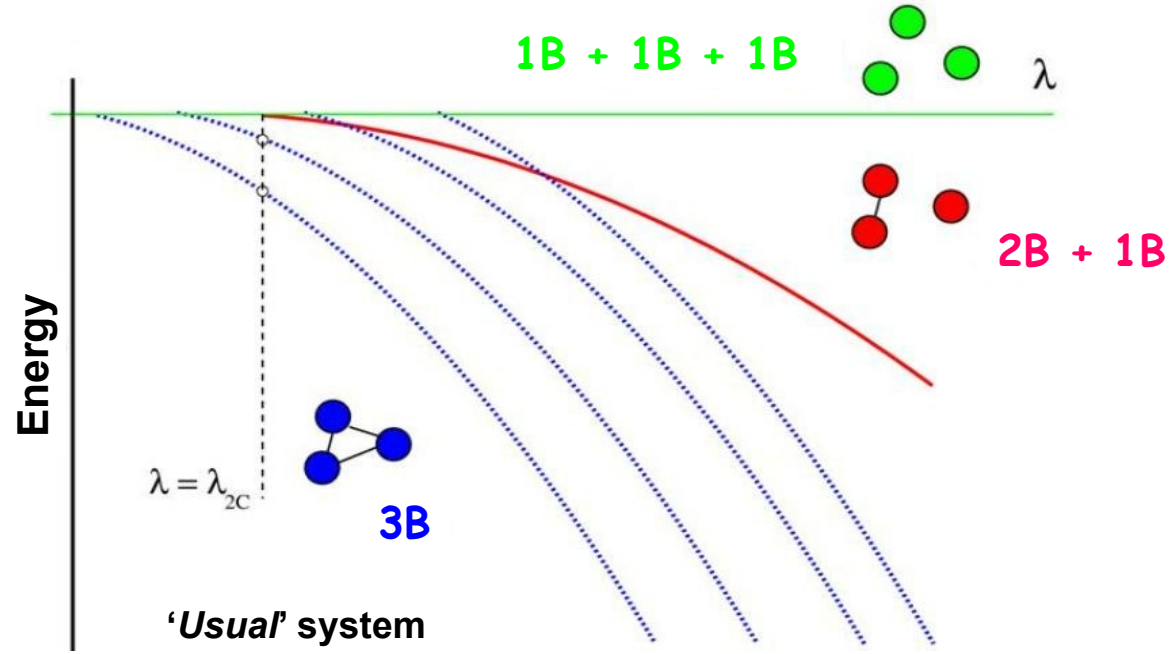
c) The masses verify certain relations

$a = 100.13$ Å

$r_0 = 7.35$ Å

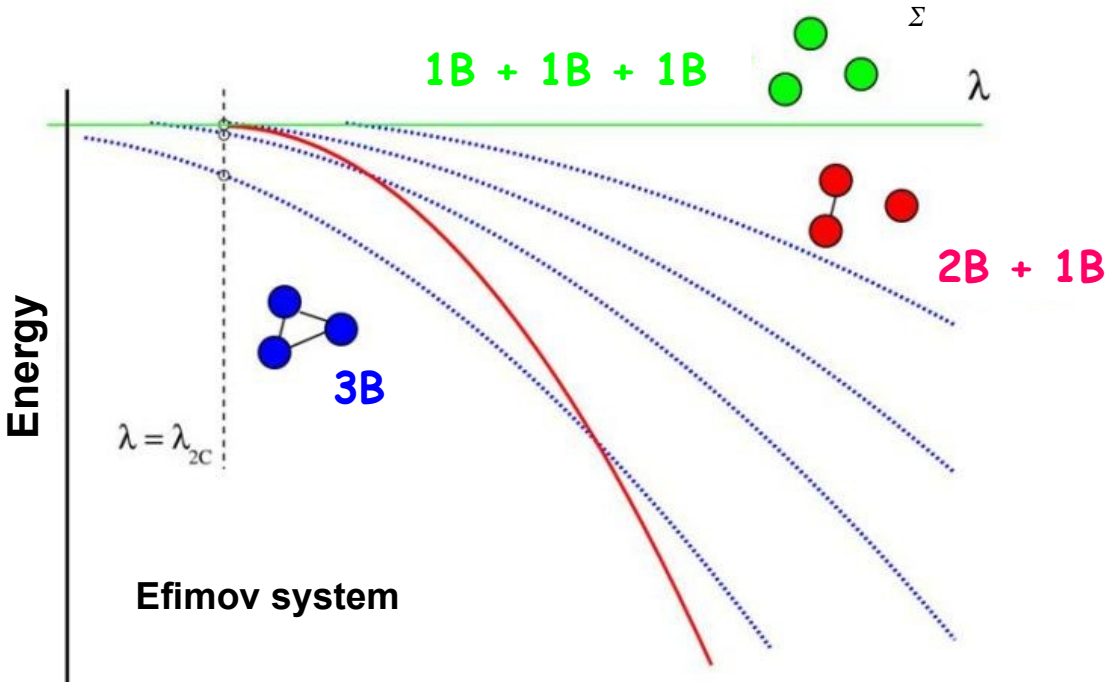
$m_1/m_2 \approx 0.8$

$V_{123}(r_1,r_2,r_3) + V_{12}(r_1) + V_{13}(r_2)$



$V_{3B}(r) = \Sigma\, \lambda V_{2B}(r)$

3B bound states appear through the **2B** threshold as λ increases



3B bound states disappear through the **2B** threshold as λ increases:

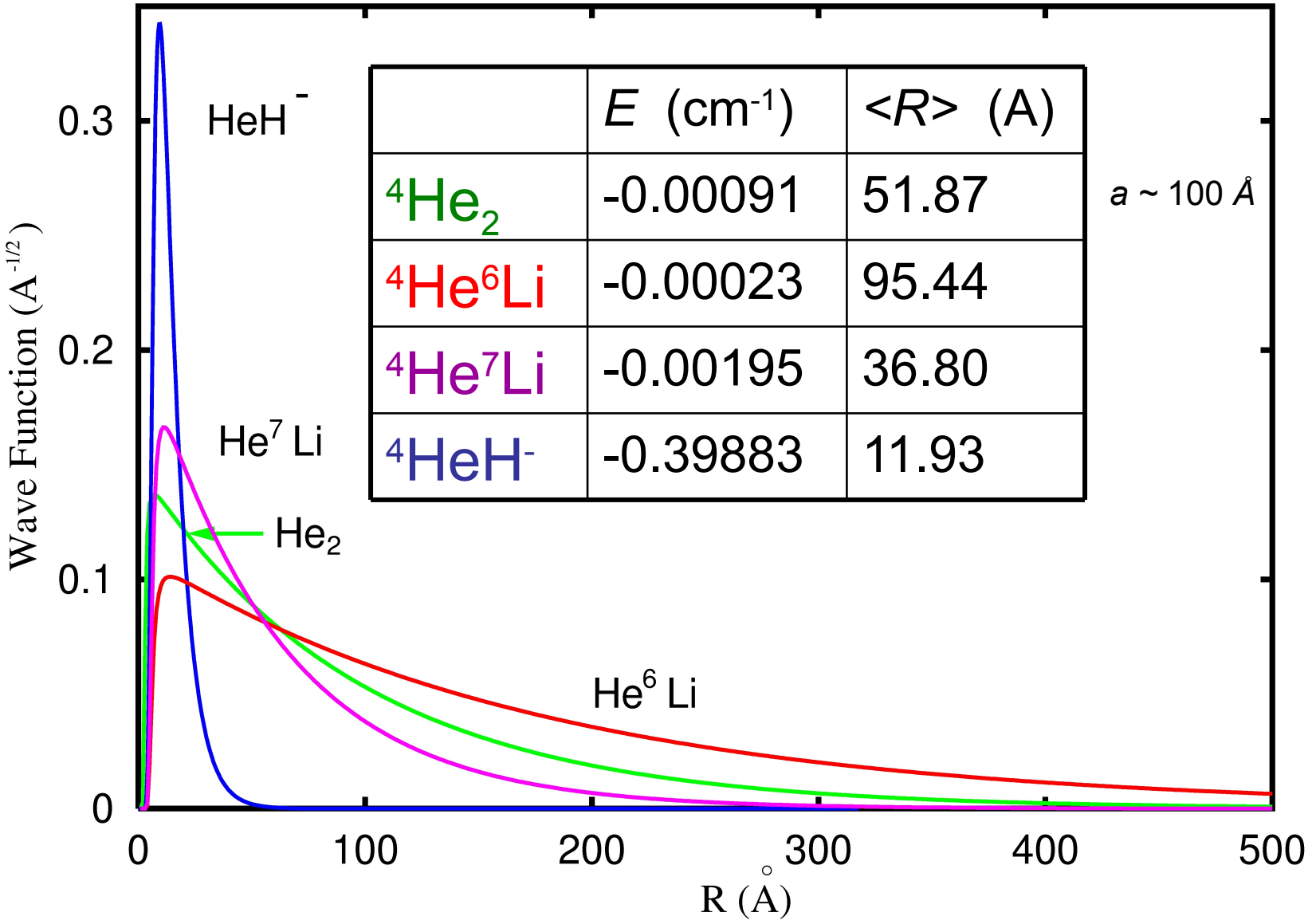
$$N = \frac{1}{\pi} \ln \frac{|a|}{r_0}$$

For He_3, for example,

$a = 100.13$ Å
$r_0 = 7.35$ Å

$N \approx 0.8$

Candidates in Molecular Physics



	E (cm^{-1})	$\langle R \rangle$ (A)
$^4He_2$	-0.00091	51.87
$^4He^6Li$	-0.00023	95.44
$^4He^7Li$	-0.00195	36.80
$^4HeH^-$	-0.39883	11.93

$a \sim 100$ Å

$^4He_3$

Barletta, Kievsky (2001)
Motovilov, Sofianos, Kolganova (1997, 1998)
Blume, Esry, Greene, Esry (1999, 2000)
Nielsen, Fedorov, Jensen (1998)
Bressanini, Zavaglia, Mella, Morosi (2000)
González-Lezana, Rubayo-Soneira, Miret-Artés, Delgado-Barrio, Gianturco, Villarreal (1999, 2000)

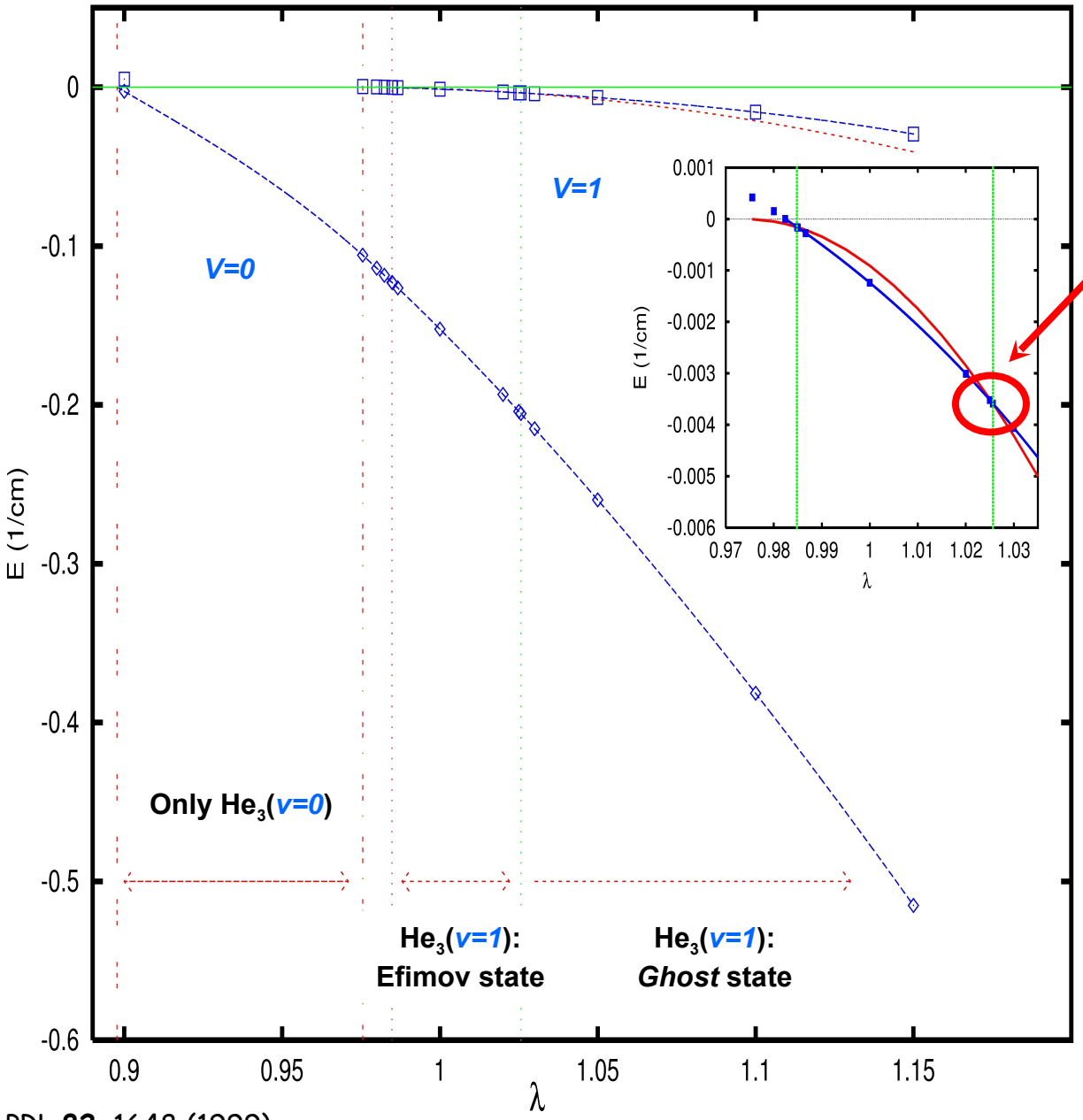
$^4He_2Li$

Yuan, Lin (1998)
Delfino, Frederico, Tomio (2000)
Baccarelli, González-Lezana, Miret-Artés, Delgado-Barrio, Gianturco, Villarreal (2000)

$^4He_2H^-$

Casalegno, Mella, Morosi, Bressanini (2000)
González-Lezana, Miret-Artés, Delgado-Barrio, Gianturco, Villarreal (2000)

He_3

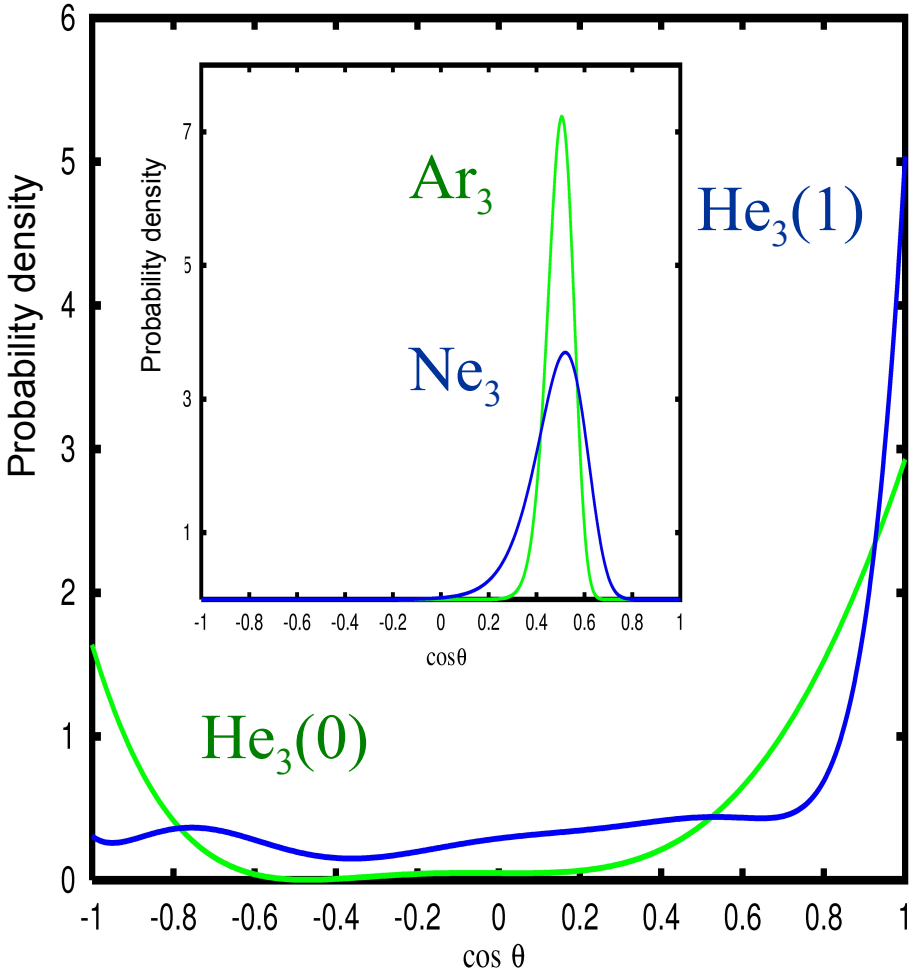


Efimov state!

T. González-Lezana et al. PRL **82**, 1648 (1999)

3. Geometrical structure

Probability density functions



Significant differences between the geometrical features of the extremely floppy He_3 system and the more localised Ar and Ne trimers.

T. González-Lezana et al. JCP **110**, 9000 (1999)

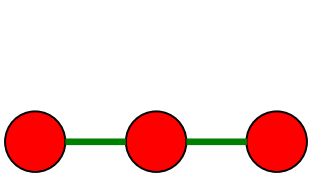
Pseudo-weights

Definition : $$1 = \langle \Phi_k | \Phi_k \rangle = \sum_j a_j^{(k)} \langle \Phi_k | \phi_j \rangle = \sum_j P_j^{(k)}$$

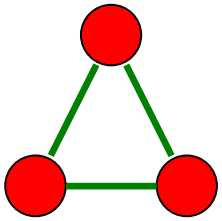
1. Alternative way to calculate of geometrical magnitudes such as average values for the area, distances ...

$$\langle x^n \rangle_k = \sum_j a_j^{(k)} \langle \Phi_k | x^n | \phi_j \rangle \approx \sum_j P_j^{(k)} x_j^n$$

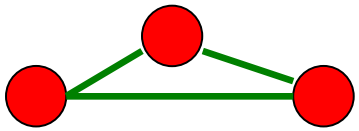
2. Analysis of the participation of different triangular arrangements on the average geometry of the system:



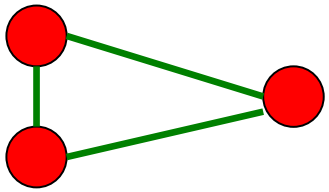
Collinear

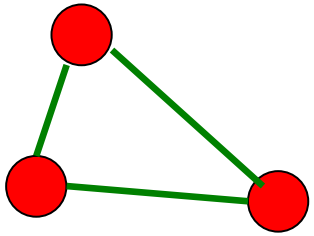


Equilateral



Isosceles



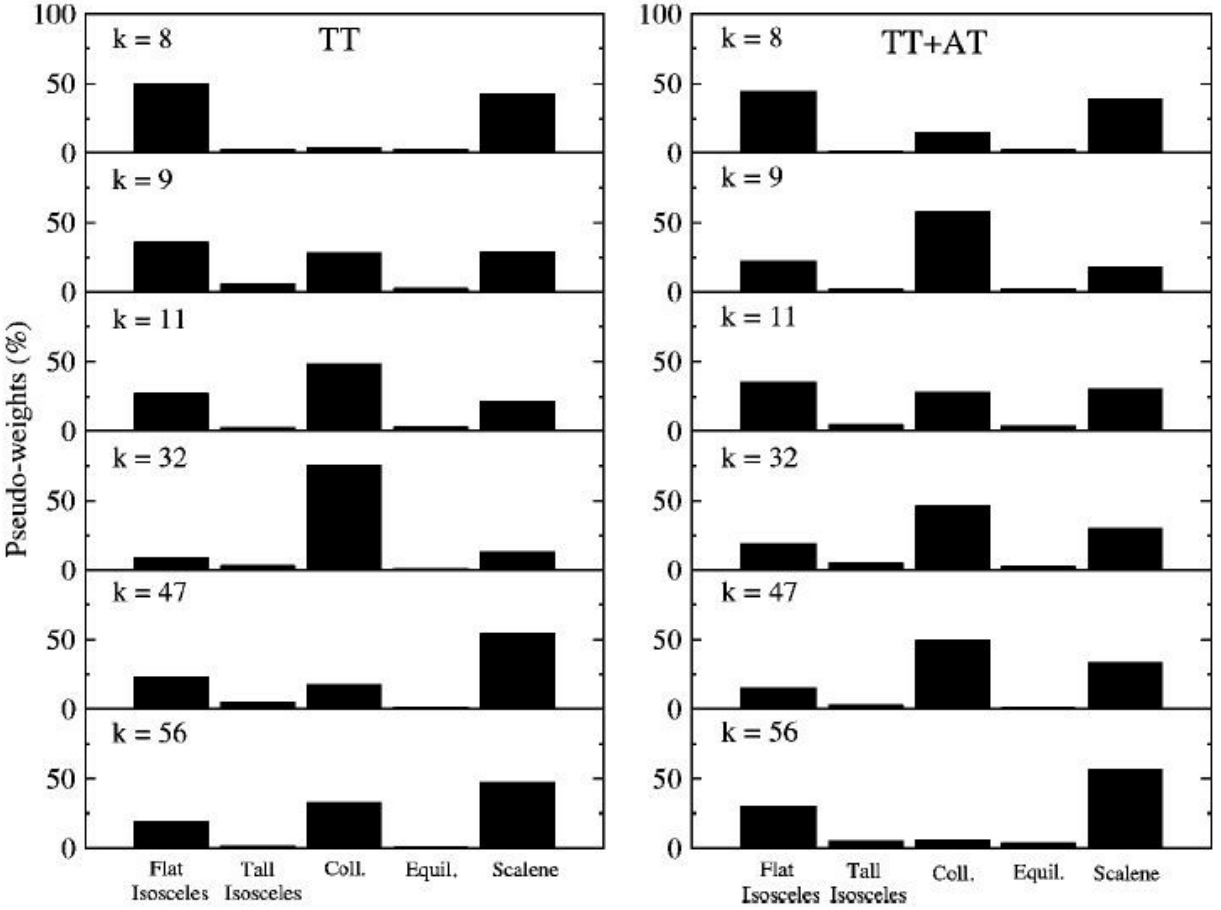


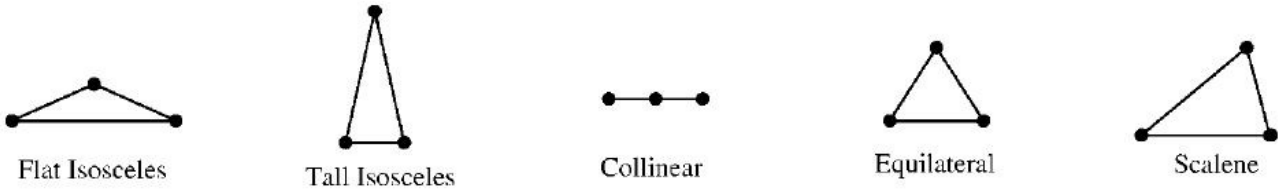
Scalene

Pseudo-weights

$$U_{DDD}(1,2,3) = \frac{3C_{DDD}}{R_1^3\, R_2^3\, R_3^3}(1 + 3\cos\phi_1 \cos\phi_2 \cos\phi_3).$$

Ar_3

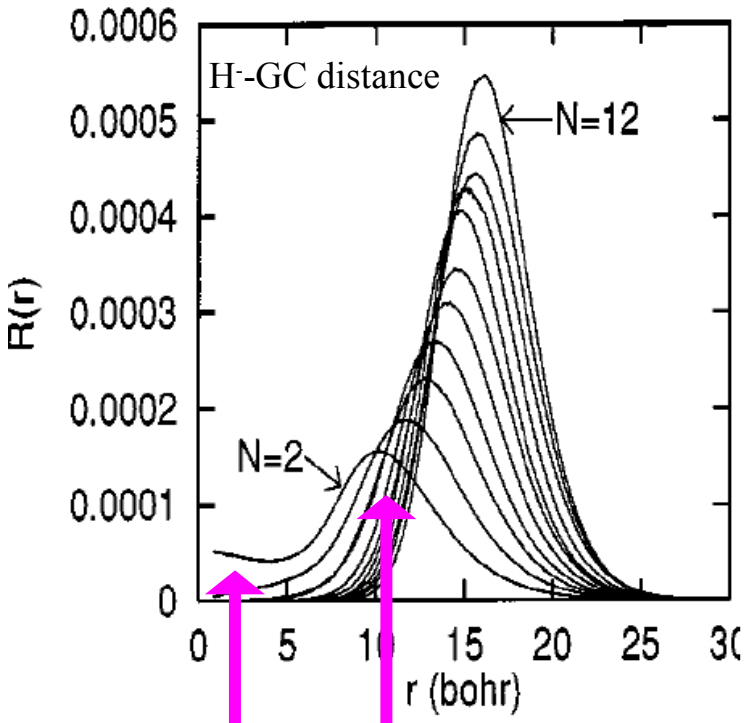




Pseudo-weights

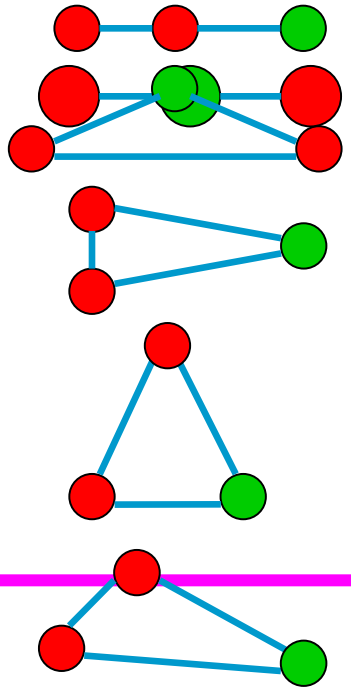
He_2H^-

M. Casalegno et al. JCP **112**, 69 (2000)



of H^- decreases in a fairly monotonic fashion. The only exception to this behavior is the smallest cluster $^4He_2H^-$; its distribution shows a rise beyond statistical fluctuation for a distance from the center less than the minimum located around 4.1 bohr. This result indicates that in the $^4He_2H^-$ cluster the linear geometry where H^- lies between the He atoms plays a significant role although H^- has a larger probability to lie 10 bohr away from the center of the cluster.

Configurations in our basis set with the larger values of $P^{(k)}_j$



r(H⁻-GC) = 13.2 bohr

r(H⁻-GC) = 2.7-4.8 bohr

r(H⁻-GC) = 10.1 bohr

r(H⁻-GC) = 10.7 bohr

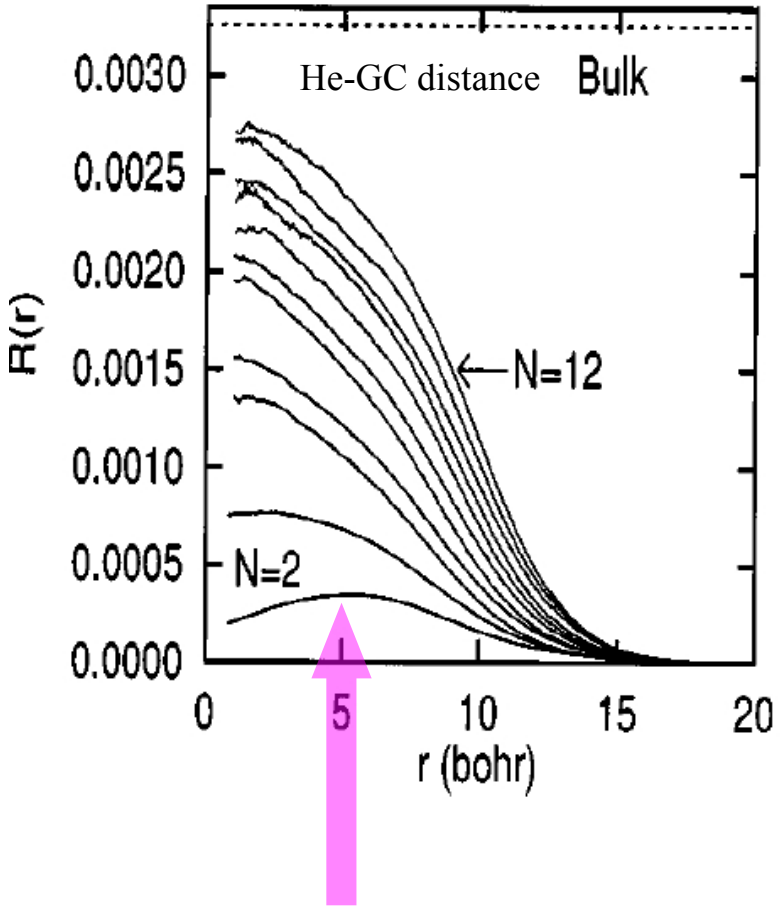
r(H⁻-GC) = 9.2 bohr

r(H⁻-GC) = 10.8 bohr

Pseudo-weights

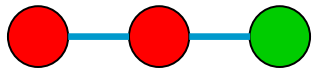
He_2H^-

M. Casalegno et al. JCP **112**, 69 (2000)



three-body cluster, i.e., $^4He_2H^-$. The He density distribution for this cluster shows a maximum around 5.30 bohr, but there is no trace of the rise of the density for small distances from the center that can be seen in the case of $^4He_3$. Nevertheless, the plot of Fig. 4 shows that He can occupy the geometrical center position, i.e., $^4He_2H^-$ in its ground state can be found in the linear geometry where the H^- ion is external to the $^4He_2$ moiety. Increasing the number of He

Configurations in our basis set with the larger values of $P^{(k)}_j$



r(He-GC) = 3.8-5 bohr

4. Rovibrational spectrum for J>0

General procedure

We assume: $H_{tot} = H_{vib} + H_{rot}.$

For an asymmetric rotor: $H_{rot} = \frac{1}{2}(A+C)\mathbf{J}^2 + \frac{1}{2}(A-C)H(\kappa)$

$$H(\kappa) = J_A^2 + \kappa J_B^2 - J_C^2 \qquad \kappa = (2B - A - C)/(A - C)$$

With the symmetry-adapted rovibrational basis:

$$|\, k; sJ\ |\Omega|\ M\rangle = \frac{1}{\sqrt{2}}\{|\ k; J\Omega M\rangle + (-1)^s\ |\ k; J\ -\Omega M\rangle\}$$

$$\Phi_k = \sum_j a_j^{(k)} \phi_j = \sum_j a_j^{(k)} N_{lmn}^{-1/2} \sum_{P \in S_3} P[\varphi_l(R_1)\varphi_m(R_2)\varphi_n(R_3)]$$

we construct the Hamiltonian matrix:

$$\langle k; J\Omega M \mid H_{rot} \mid k'; J'\Omega' M' \rangle = \sum_{jj'} a_j^{(k)} a_{j'}^{(k)} \langle \phi_j; J\Omega M \mid H_{rot} \mid \phi_{j'}; J'\Omega' M' \rangle$$

?

General procedure

$$\langle \varphi_l \varphi_m \varphi_n ; J\Omega M \,|\, H_{rot} \,|\, \varphi_{l'} \varphi_{m'} \varphi_{n'} ; J'\Omega' M' \rangle \approx \langle J\Omega M \,|\, H_{rot}(R_1^\dagger, R_2^\dagger, R_3^\dagger) \,|\, J'\Omega' M' \rangle s_{ll'} s_{mm'} s_{nn'}$$

depends on R_1, R_2 and R_3

$$\langle J\Omega M \;\; | \;\; H_{rot}(R_1^\dagger, R_2^\dagger, R_3^\dagger) \mid J'\Omega' M' \rangle = \frac{1}{2}(A^\dagger + C^\dagger) J(J+1) \delta_{J,J'} \delta_{\Omega,\Omega'} \delta_{M,M'} + \frac{1}{2}(A^\dagger - C^\dagger) \langle J\Omega M \mid H(\kappa) \mid J'\Omega' M' \rangle \delta_{J,J'} \delta_{M,M'}$$

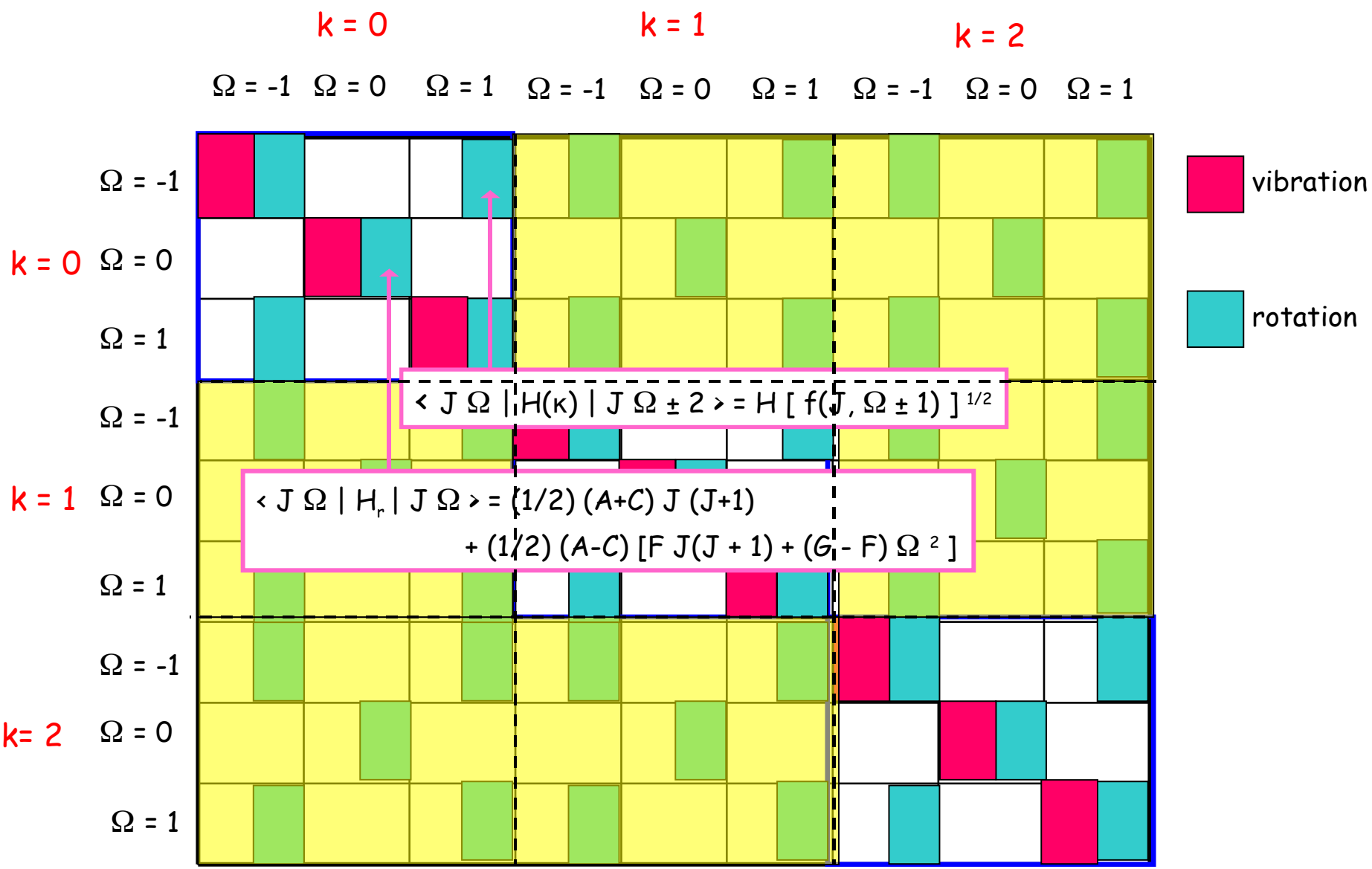
$$\langle J\Omega M \mid H(\kappa) \mid J\Omega' M \rangle = \left[\mathcal{F}^\dagger J(J+1) + (\mathcal{G}^\dagger - \mathcal{F}^\dagger)\Omega^2 \right] \delta_{\Omega,\Omega'} + \mathcal{H}^\dagger \sqrt{f(J, \Omega \pm 1)} \delta_{\Omega \pm 2, \Omega'},$$

$$f(J, \Omega \pm 1) = \frac{1}{4} \left[J(J+1) - \Omega(\Omega \pm 1) \right] \left[J(J+1) - (\Omega \pm 1)(\Omega \pm 2) \right]$$

$$\mathcal{F} = (\kappa + 1)/2, \; \mathcal{G} = -1 \;\; \mathcal{H} = (\kappa - 1)/2$$

$R_1^\dagger, R_2^\dagger, R_3^\dagger$ ⇒ $A^\dagger \;\; B^\dagger \;\; C^\dagger \;\; \mathcal{F}^\dagger \;\; \mathcal{G}^\dagger \;\; \mathcal{H}^\dagger$ ⇒ $H_{rot}(R_1^\dagger, R_2^\dagger, R_3^\dagger)$

Let's suppose J = 1, Ω = -1,0,1 and three vibrational states k = 0, 1, 2



Ar_3

J=0

HC [1]		HC (this work)		DGF	
$(v_1,v_2^{\,l})$ (L,K)	E [cm^{-1}]	$(v_1,v_2^{\,l})(\Omega)\,\Gamma$	E [cm^{-1}]	(k,Ω,Γ)	E [cm^{-1}]
$(0,0^0)(0,0)$	**-252.24**	$(0,0^0)(0)A_1'$	**-252.23**	(1,0,III)	**-252.23**
		$(0,1^1)(0)E'$	-229.78	(2-3,0,II-I)	-229.79
$(1,0^0)(0,0)$	**-221.80**	$(1,0^0)(0)A_1'$	**-221.79**	(4,0, III)	**-221.79**
$(0,2^0)(0,0)$	**-209.48**	$(0,2^0)(0)A_1'$	**-209.48**	(5,0, III)	**-209.48**
		$(0,2^2)(0)E'$	-209.32	(6-7,0,II-I)	-209.33
		$(1,1^1)(0)E'$	-202.58	(8-9,0,II-I)	-202.58
$(2,0^0)(0,0)$	**-195.99**	$(2,0^0)(0)A_1'$	**-195.97**	(10,0, III)	**-195.98**
		$(1,1^1)(0)E'$	-193.21	(11-12,0,II-I)	-193.22
	-191.29	$(2,1^0)(0)A_1'$	**-191.29**	(13,0, III)	**-191.28**
		$(0,3^3)(0)\,A_2'$	-187.76	(14,0, I)	-187.76

[1] F. Karlický et al. JCP **126**, 74305 (2007)

III
II
I

Assignment $l \leftrightarrow k\Omega$ for the J=0 case

$$\phi_J = N_{lmn}^{-1/2} \sum_{P \in S_3} P[\varphi_l(R_1)\,\varphi_m(R_2)\,\varphi_n(R_3)]\ )]\varphi_n(R_3)$$

Total symmetry as a product: $\Gamma = \Gamma_{\mathrm{v}}^{\Omega\ell} \times \Gamma_{\mathrm{R}}$

Symmetry-adapted vibrational functions:

$$f_n^{\Gamma_{\mathrm{v}}^{\Omega\ell}}(\phi_\tau) = A_n^{\Gamma_{\mathrm{v}}^{\Omega\ell}} \mathrm{e}^{-in\phi_\tau} + B_n^{\Gamma_{\mathrm{v}}^{\Omega\ell}} \mathrm{e}^{in\phi_\tau} \qquad n = |\pm 2\ell - \Omega|$$

Coefficients after symmetry operations of D_{3h} group:

$$A_n^{\Gamma_{\mathrm{v}}^{\Omega\ell}} = \chi^{\Gamma_{\mathrm{v}}^{\Omega\ell}}(E) + \chi^{\Gamma_{\mathrm{v}}^{\Omega\ell}}(C_3)\, 2\cos\frac{4\pi}{3}n$$

$$B_n^{\Gamma_{\mathrm{v}}^{\Omega\ell}} = \chi^{\Gamma_{\mathrm{v}}^{\Omega\ell}}(C_2)\left(1 + 2\cos\frac{2\pi}{3}n\right).$$

Practical rules:

(i) For $n = 0$, $\Gamma_{\mathrm{v}}^{\Omega\ell} = A_1$

(ii) for n multiple of 3, $\Gamma_{\mathrm{v}}^{\Omega\ell} \sim A_1$ and A_2

(iii) for n not multiple of 3, $\Gamma_{\mathrm{v}}^{\Omega\ell} = E$

Rotational symmetry: $\Gamma = \Gamma_{\mathrm{v}}^{\Omega\ell} \times \Gamma_{\mathrm{R}}$

Symmetry-adapted vibrational functions:

$$D^{J\Gamma_{\mathrm{R}}}_{M\Omega}(\alpha,\beta,\gamma) = A^{J\Gamma_{\mathrm{R}}}_{M\Omega}\, D^{J*}_{M\Omega}(\alpha,\beta,\gamma) + B^{J\Gamma_{\mathrm{R}}}_{M\Omega}\, D^{J*}_{M-\Omega}(\alpha,\beta,\gamma)$$

Coefficients after symmetry operations of D_{3h} group:

$$A^{J\Gamma_{\mathrm{R}}}_{M\Omega} = \begin{cases} \chi^{\Gamma_{\mathrm{R}}}(E) + 2\chi^{\Gamma_{\mathrm{R}}}(C_3), & \Omega \neq 0, \\ \chi^{\Gamma_{\mathrm{R}}}(E) + 2\chi^{\Gamma_{\mathrm{R}}}(C_3) + 3(-1)^J \chi^{\Gamma_{\mathrm{R}}}(C_2), & \Omega = 0, \end{cases}$$

$$B^{J\Gamma_{\mathrm{R}}}_{M\Omega} = \begin{cases} 3(-1)^{J-\Omega} \chi^{\Gamma_{\mathrm{R}}}(C_2), & \Omega \neq 0, \\ 0, & \Omega = 0, \end{cases}$$

Practical rules:

(i) for $\Omega = 0$, $\Gamma_{\mathrm{R}} = A_1$ for even values of J and $\Gamma_{\mathrm{R}} = A_2$ for odd J,

(ii) for $\Omega \neq 0$, both A_1 and A_2 representations are possible

In summary:

$$\Gamma = \Gamma_{\mathrm{v}}^{\Omega\ell} \times \Gamma_{\mathrm{R}}$$

For each value of k and Ω (and therefore l) : $n = |\pm 2\ell - \Omega|$

The symmetry for the vibrational part $\Gamma_{\mathrm{v}}^{\Omega\ell}$:

(i) For $n = 0$, $\Gamma_{\mathrm{v}}^{\Omega\ell} = A_1$

(ii) for n multiple of 3, $\Gamma_{\mathrm{v}}^{\Omega\ell} \sim A_1$ and A_2

(iii) for n not multiple of 3, $\Gamma_{\mathrm{v}}^{\Omega\ell} = E$

The symmetry for the rotational part Γ_{R} :

(i) for $\Omega = 0$, $\Gamma_{\mathrm{R}} = A_1$ for even values of J and $\Gamma_{\mathrm{R}} = A_2$ for odd J,

(ii) for $\Omega \neq 0$, both A_1 and A_2 representations are possible

Ar_3

J=6

Γ	HC		DGF				
	(v_1, v_2^{ℓ})	$E\,(cm^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E\,(cm^{-1})$
A_2'	$(0,0^0)$	−250.85	1	6	A_1,A_2	A_2,A_1	−250.85
	$(0,1^1)$	−227.68	2,3	4	A_1,A_2	A_2,A_1	−227.86
	$(0,1^1)$	−227.56	2,3	2	A_1,A_2	A_2,A_1	−227.54
	$(1,0^0)$	−220.46	4	6	A_1,A_2	A_2,A_1	−220.46
A_2''	$(0,0^0)$	−250.06	1	3	A_1,A_2	A_2,A_1	−250.06
	$(0,1^1)$	−228.35	2,3	5	A_1,A_2	A_2,A_1	−228.12
	$(0,1^1)$	−227.29	2,3	1	A_1,A_2	A_2,A_1	−227.36
	$(1,0^0)$	−219.68	4	3	A_1,A_2	A_2,A_1	−219.69
E'	$(0,0^0)$	−250.26	1	4	E	A_1,A_2	−250.27
	$(0,0^0)$	−249.91	1	2	E	A_1,A_2	−249.92
	$(0,1^1)$	−228.13	2,3	6	E	A_1,A_2	−228.44
	$(0,1^1)$	−228.03	2,3	4	E	A_1,A_2	−227.86
	$(0,1^1)$	−227.46	2,3	2	E	A_1,A_2	−227.50
	$(0,1^1)$	−227.32	2,3	0	E	A_1	−227.36
E''	$(0,0^0)$	−250.53	1	5	E	A_1,A_2	−250.53
	$(0,0^0)$	−249.83	1	1	E	A_1,A_2	−249.83
	$(0,1^1)$	−227.88	2,3	5	E	A_1,A_2	−228.12
	$(0,1^1)$	−227.77	2,3	3	E	A_1,A_2	−227.66
	$(0,1^1)^a$	−227.54	2,3	3	E	A_1,A_2	−227.66
	$(0,1^1)^a$	−227.41	2,3	1	E	A_1,A_2	−227.46
	$(1,0^0)^a$	−220.14	4	5	E	A_1,A_2	−220.14
	$(1,0^0)$	−219.46	4	1	E	A_1,A_2	−219.49

Γ	HC		DGF				
	(v_1, v_2^{ℓ})	$E\,(cm^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E\,(cm^{-1})$
A_1'	$(0,0^0)$	−250.85	1	6	A_1,A_2	A_1,A_2	−250.85
	$(0,0^0)$	−249.80	1	0	A_1	A_1	−249.80
	$(0,1^1)$	−227.68	2,3	4	A_1,A_2	A_1,A_2	−227.86
	$(0,1^1)$	−227.56	2,3	2	A_1	A_1,A_2	−227.54
	$(1,0^0)$	−220.46	4	6	A_1,A_2	A_1,A_2	−220.46
	$(1,0^0)$	−219.43	4	0	A_1	A_1	−219.40
	$(0,2^0)$	−208.17	5	6	A_1,A_2	A_1,A_2	−208.17
	$(0,2^2)$	−207.69	6,7	4	A_1,A_2	A_1,A_2	−207.48
	$(0,2^0)$	−207.22	5	0	A_1	A_1	−206.94
	$(0,2^2)$	−206.84	6,7	2	A_1,A_2	A_1,A_2	−207.05
A_1''	$(0,0^0)$	−250.06	1	3	A_1,A_2	A_1,A_2	−250.06
	$(0,1^1)$	−228.35	2,3	5	A_1,A_2	A_1,A_2	−228.12
	$(0,1^1)$	−227.43	2,3	1	A_1,A_2	A_1,A_2	−227.36
	$(1,0^0)$	−219.68	4	3	A_1,A_2	A_1,A_2	−219.69
	$(0,2^0)$	−207.48	5	3	A_1,A_2	A_1,A_2	−207.48
	$(0,2^2)$	−207.33	6,7	5	A_1,A_2	A_1,A_2	−207.72
	$(0,2^2)$	−207.09	6,7	1	A_1,A_2	A_1,A_2	−207.05
	$(1,1^1)$	−201.00	8,9	5	A_1,A_2	A_1,A_2	−200.97
	$(1,1^1)$	−200.28	8,9	1	A_1,A_2	A_1,A_2	−200.14
	$(2,0^0)$	−193.93	10	3	A_1,A_2	A_1,A_2	−193.95

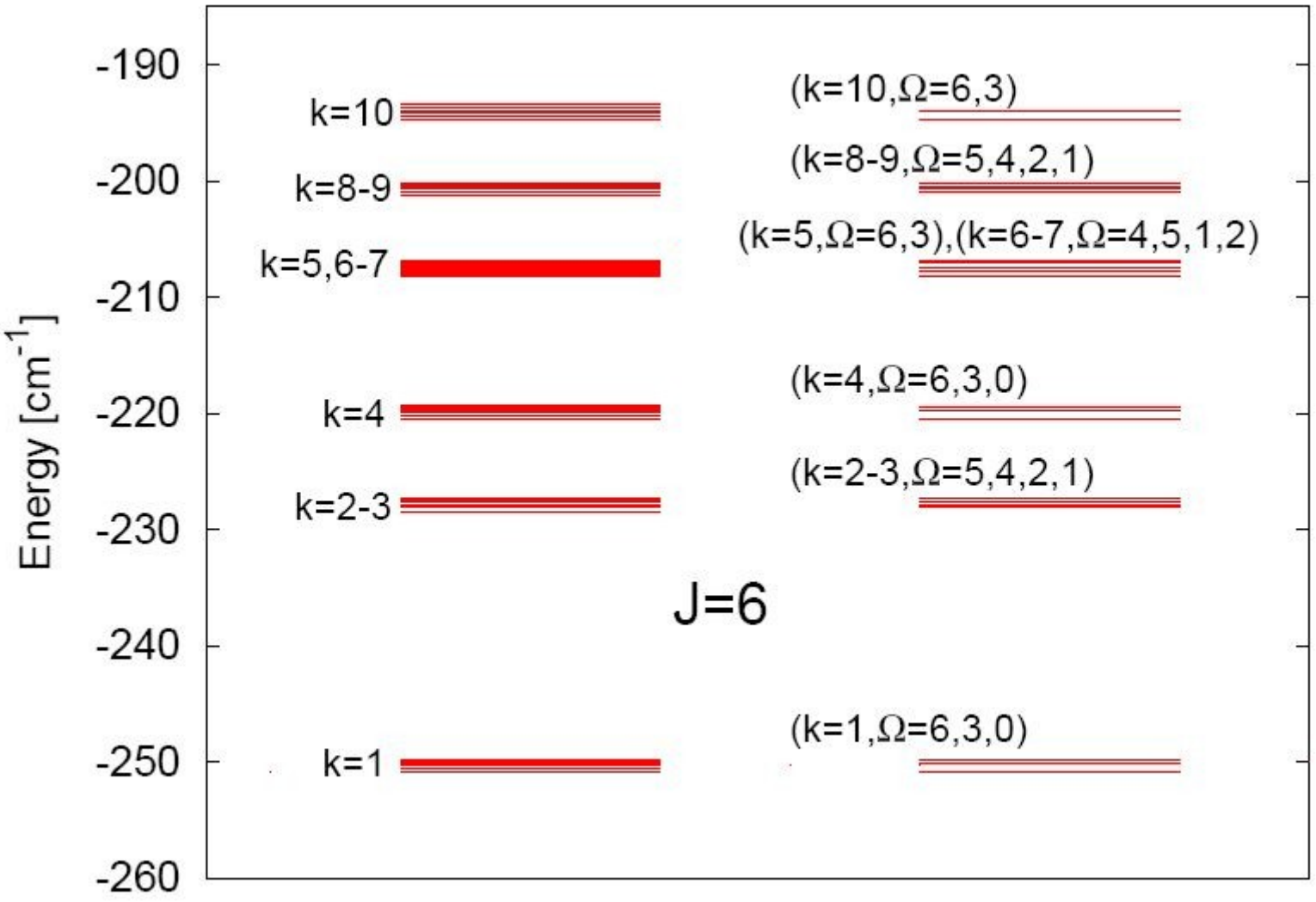
Largest HC-DGF energy difference: ***≤ 0.4 cm^{-1}***

Ar_3

HC (this work)		DGF	
$(v_1, v_2^\ell)(\Omega)\Gamma$	$E(cm^{-1})$	$(k,\Omega,s,\overline{\Gamma})$	$E(cm^{-1})$
$(0,0^0)(15)\ A_1''$	-244.89	$(1,15,III)$	-244.91
$(0,0^0)(13)\ A_1'$	-242.53	$(1,13,III)$	-242.55
$(0,0^0)(9)\ A_1''$	-240.71	$(1,9,III)$	-240.71
$(0,0^0)(6)\ A_1'$	-239.41	$(1,6,III)$	-239.40
$(0,0^0)(3)\ A_1''$	-238.63	$(1,3,III)$	-238.62
$(0,1^1)(14)\ A_1'$	-222.47	$(2/3,14,II/I)$	-221.81
$(0,1^1)(13)\ A_1''$	-220.44	$(2/3,13,II/I)$	-221.03
$(0,1^1)(11)\ A_1''$	-220.06	$(2/3,11,II/I)$	-219.64
$(0,1^1)(10)\ A_1'$	-218.72	$(2/3,10,II/I)$	-219.04
$(0,1^1)(8)\ A_1'$	-218.16	$(2/3,8,II/I)$	-218.00
$(0,1^1)(7)\ A_1''$	-217.50	$(2/3,7,II/I)$	-217.58
$(0,1^1)(5)\ A_1''$	-216.80	$(2/3,5,II/I)$	-216.91
$(0,1^1)(4)\ A_1'$	-216.76	$(2/3,4,II/I)$	-216.63
$(0,1^1)(2)\ A_1'$	-215.97	$(2/3,2,II/I)$	-216.06
$(0,1^1)(1)\ A_1''$	-215.72	$(2/3,1,II/I)$	-215.72
$(1,0^0)(15)\ A_1''$	-214.69	$(4,15,III)$	-214.71

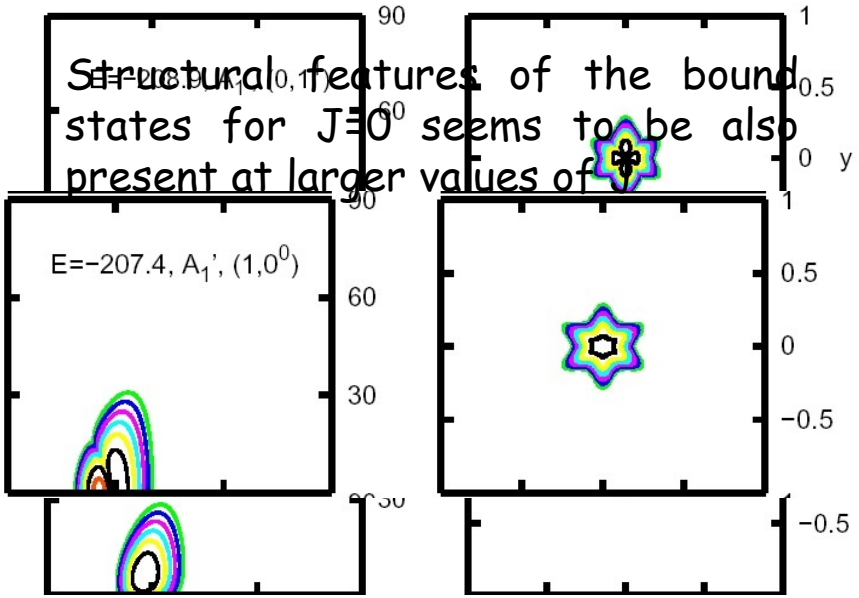
J=15

Largest HC-DGF energy difference: ***≤ 0.6 cm^{-1}***


-190
-200
-210
-220
-230
-240
-250
-260
Energy [cm-1]
k=10
k=8-9
k=5,6-7
k=4
k=2-3
k=1
(k=10,Ω=6,3)
(k=8-9,Ω=5,4,2,1)
(k=5,Ω=6,3),(k=6-7,Ω=4,5,1,2)
(k=4,Ω=6,3,0)
(k=2-3,Ω=5,4,2,1)
(k=1,Ω=6,3,0)
J=6

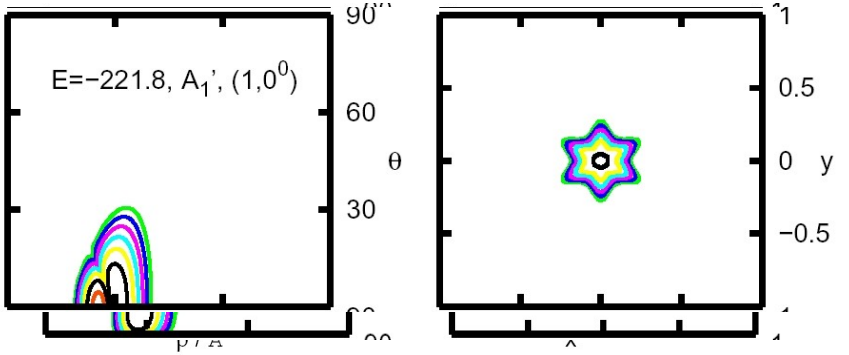
J=20

Ar_3



Structural features of the bound states for J=0 seems to be also present at larger values of J

J=0



HC (this work)		DGF	
$(v_1, v_2^\ell)(\Omega)\Gamma$	$E(cm^{-1})$	$(k,\Omega,s,\overline{\Gamma})$	$E(cm^{-1})$
$(0,0^0)(18)\ A_1'$	-237.36	(1,18,III)	-237.39
$(0,0^0)(15)\ A_1''$	-234.50	(1,15,III)	-234.51
$(0,0^0)(12)\ A_1'$	-232.17	(1,12,III)	-232.15
$(0,0^0)(9)\ A_1''$	-230.36	(1,9,III)	-230.32
$(0,0^0)(6)\ A_1'$	-229.08	(1,6,III)	-229.01
$(0,0^0)(3)\ A_1''$	-228.31	(1,3,III)	-228.24
$(0,0^0)(0)\ A_1'$	-228.05	(1,0,III)	-227.91
$(0,1^1)(20)\ A_1'$	-218.43	(2/3,20,II/I)	-217.49
$(0,1^1)(19)\ A_1''$	-215.44	(2/3,19,II/I)	-216.36
$(0,1^1)(17)\ A_1''$	-215.00	(2/3,17,II/I)	-214.28
$(0,1^1)(16)\ A_1'$	-212.73	(2/3,16,II/I)	-213.33
$(0,1^1)(14)\ A_1'$	-212.02	(2/3,14,II/I)	-211.60
$(0,1^1)(13)\ A_1''$	-210.55	(2/3,13,II/I)	-210.83
$(0,1^1)(11)\ A_1''$	-209.59	(2/3,11,II/I)	-209.46
$(0,1^1)(10)\ A_1'$	-208.87	(2/3,10,II/I)	-208.86
$(0,1^1)(8)\ A_1'$	-207.71	(2/3,8,II/I)	-207.86
$(0,1^1)(7)\ A_1''$	-207.68	(2/3,7,II/I)	-207.44
$(1,0^0)(18)\ A_1'$	-207.38	(4,18,III)	-207.41
$(0,1^1)(2)\ A_1'$	-206.99	(2/3,2,II/I)	-207.17

Rotational constants

	DGF				HC[1]			
k	A [MHz]	B [MHz]	B' [MHz]	C [MHz]	(v_1,v_2^{ℓ})	B [MHz]	C [MHz]	rms
1	1739.26	1739.17	1739.21	861.32	$(0,0^0)$	1738.35	863.32	2×10^{-4}
2-3	1713.43	1712.97	1713.20	837.77	$(0,1^1)$	1697.59	785.88	3×10^{-2}
4	1692.88	1692.07	1692.48	831.62	$(1,0^0)$	1691.92	834.58	1×10^{-4}
5	1688.91	1688.22	1688.57	812.15	$(0,2^0)$	1596.78	809.92	1×10^{-2}
6-7	1688.16	1686.76	1687.46	809.40	$(0,2^2)$	1694.31	627.73	7×10^{-2}
8-9	1672.23	1666.65	1669.44	806.15	$(1,1^1)$	1630.11	644.37	1×10^{-1}
10	1672.66	1660.20	1666.43	782.32	$(2,0^0)$	1653.20	782.53	2×10^{-3}
11-12	1688.71	1660.45	1674.46	771.56	$(0,3^1)$	1601.10	541.76	1×10^{-1}

[1] F. Karlický et al. JCP **126**, 74305 (2007)

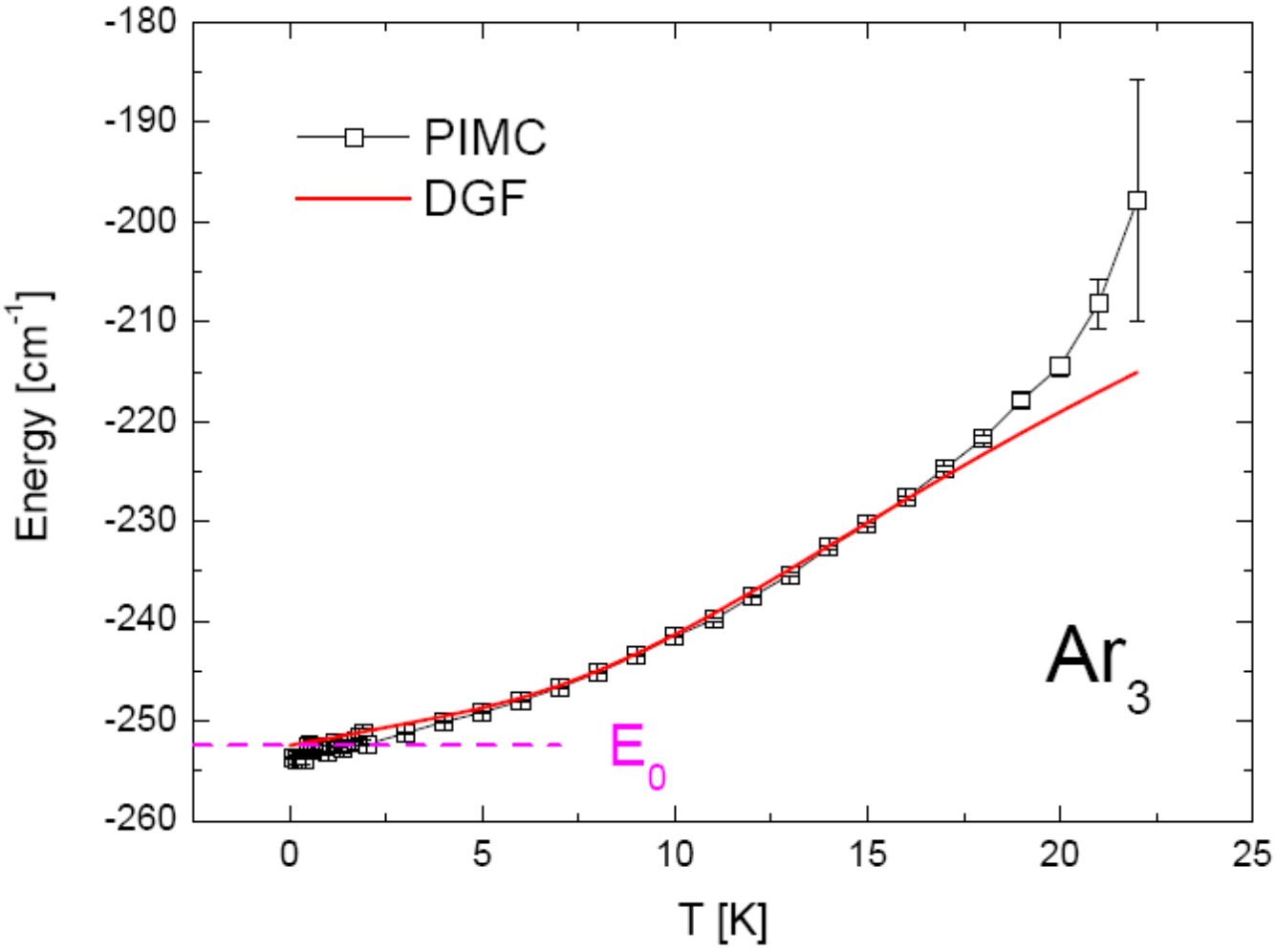
$$\epsilon^{JKL}_{v_1v_2\ell} = \epsilon^{00L=2\ell}_{v_1v_2\ell} + B_{v_1v_2\ell}[J(J+1)-K^2] + C_{v_1v_2\ell}LK$$

Adjustable parameters

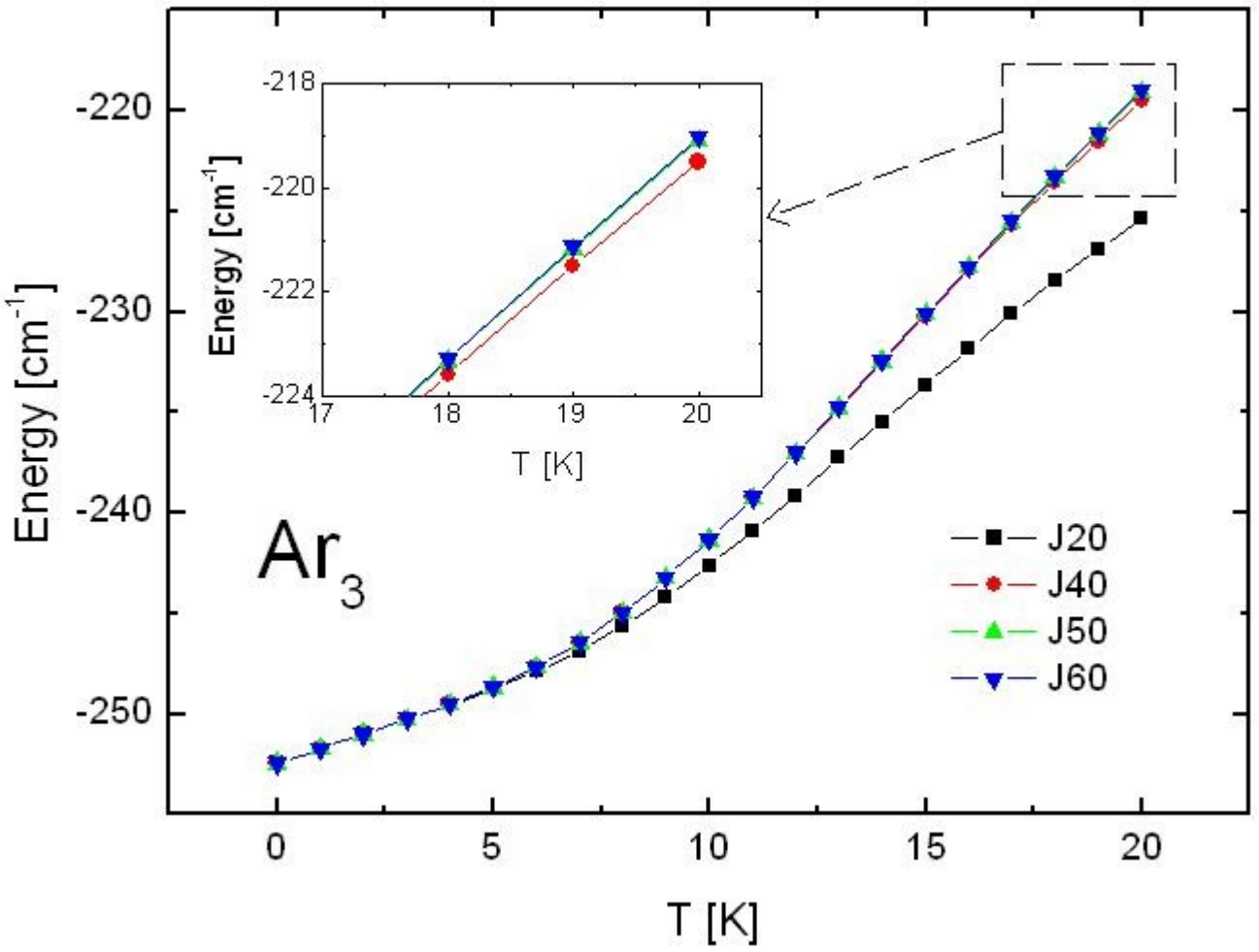
Variables

state energies. For each set of the three quantum numbers (v_1, v_2^{ℓ}), we treat Eq. (16) as a linear equation with two variables, $J(J+1)-K^2$ and LK, and adjust the three remaining constants, $\epsilon^{00L=2\ell}_{v_1v_2\ell}$, $B_{v_1v_2\ell}$, and $C_{v_1v_2\ell}$, to minimize the root mean square deviation between the sets of exact eigenvalues and the approximate ones given by Eq. (16). The results are

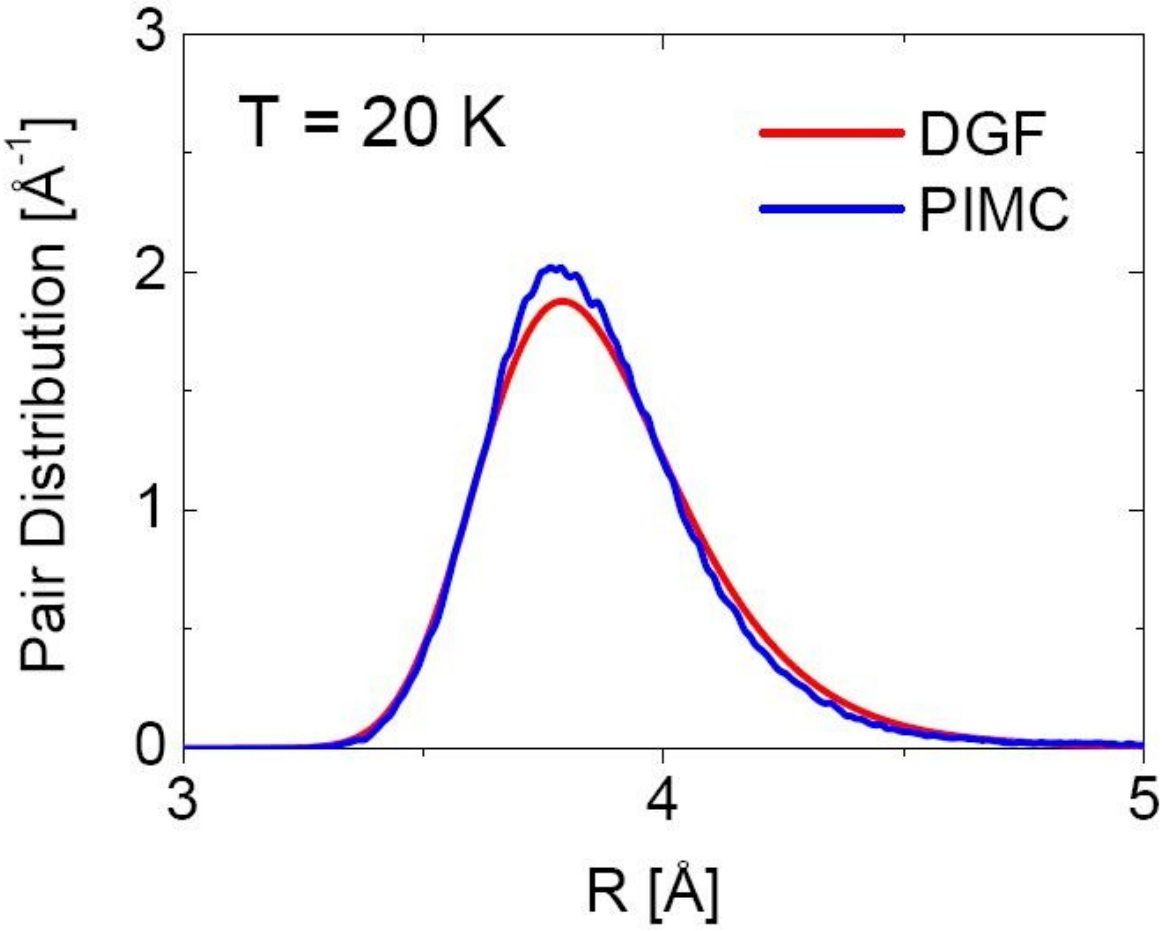
$$E(T) = \frac{\sum_{kJ\Omega} \exp(-E_{kJ\Omega} / KT) E_{kJ\Omega}}{\sum_{kJ\Omega} \exp(-E_{kJ\Omega} / KT)}$$

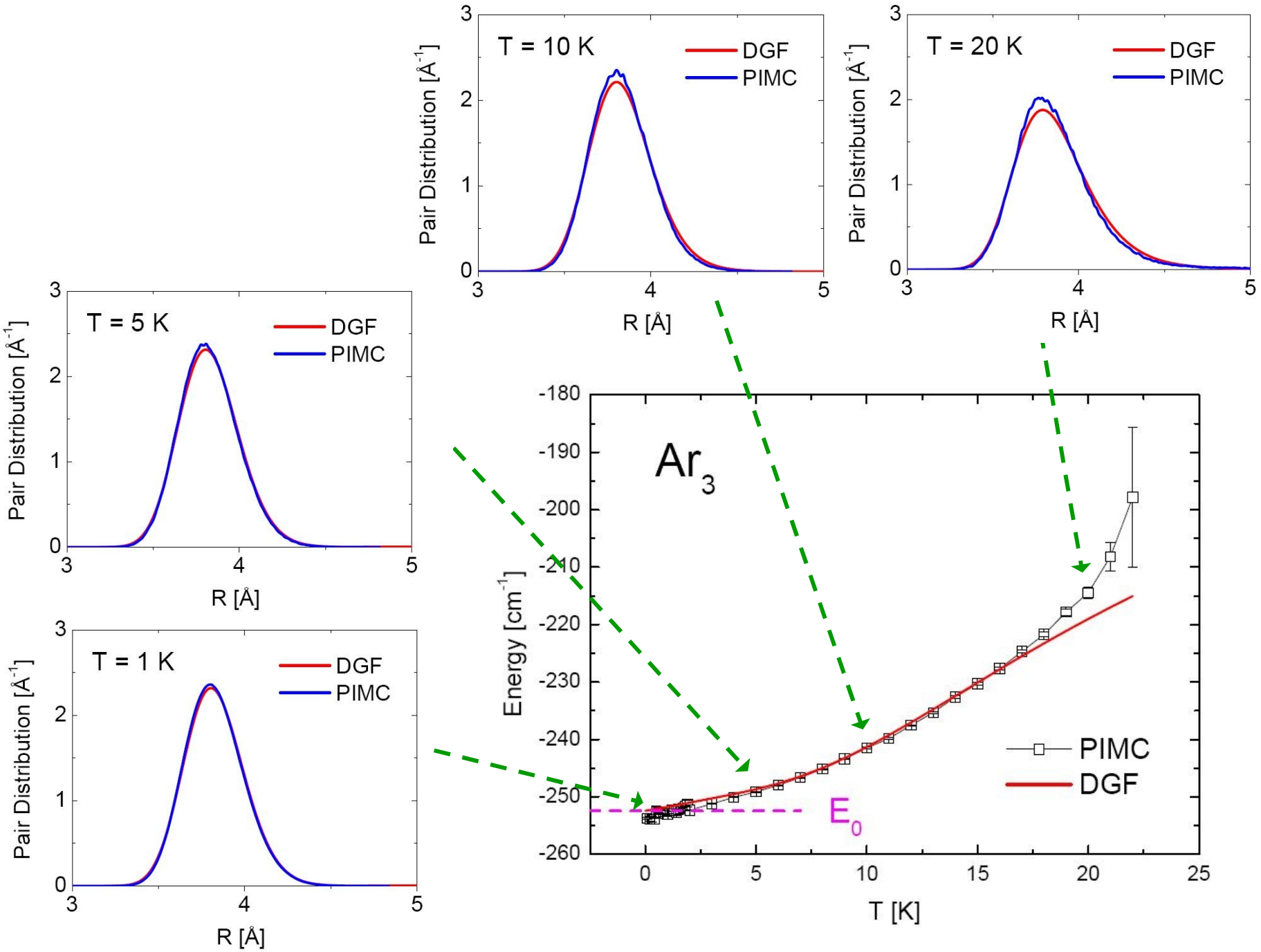


Need of a large number of J-partial waves to ensure convergence in terms of T



$$D(R;T)=\frac{\sum_{kJ\Omega}\exp\left(-E_{kJ\Omega}/KT\right)D_{k\Omega}^{J=0}(R)}{\sum_{kJ\Omega}\exp\left(-E_{kJ\Omega}/KT\right)}$$




T = 10 K
DGF
PIMC
Pair Distribution [Å^{-1}]
R [Å]
T = 20 K
DGF
PIMC
Pair Distribution [Å^{-1}]
R [Å]
T = 5 K
DGF
PIMC
Pair Distribution [Å^{-1}]
R [Å]
T = 1 K
DGF
PIMC
Pair Distribution [Å^{-1}]
R [Å]
Ar$_3$
Energy [cm^{-1}]
T [K]
PIMC
DGF
E$_0$

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Vibrational and rotational bound states in floppy triatomic systems: The distributed Gaussian functions approach

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Symmetry assignment in the distributed Gaussian functions method to study homonuclear rotating trimers

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Conclusions

- The DGF method constitutes a reliable approach to study the vibrational spectrum and geometrical structure of different three body molecular systems.

- An approximate procedure based on the DGF method has been proposed to study the rovibrational spectrum of rotating trimers. Energy levels predicted by means of this method for the Ar_3 system are in a fairly good accord with results of exact hyperspherical coordinate calculations even for large values of the total angular momentum (J = 20).

- Future applications to other trimers will enable to test its possible limitations.