Supporting Information

Thermal and Pressure Response of

KHg(CN)₂(SCN)

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Crystal Micrograph of KHg(CN)₂(SCN)

Figure S1 represents the prepared colorless single crystal optical image of the compound KHg(CN)₂(SCN) captured under transmission geometry employing in-house stereo microscope SMZ1000.



Figure S1: Crystal Micrograph of KHg(CN)₂(SCN)

FTIR Spectroscopy

Figure S2 shows the FTIR spectra for KHg(CN)₂(SCN) at ambient condition recorded in the range 4000 to 500 cm⁻¹ with spatial resolution of 4 cm⁻¹ using the 15x objective in transmission geometry. The measurement was performed using Vertex 80 FTIR spectrometer attached with 3000 Hyperion Microscope and Deuterated triglycine sulfate (DTGS) detector. The prominent observed modes are C-S stretching mode at 735 cm⁻¹,^{1, 2} overtone of S-C \equiv N bending modes at 886 cm⁻¹ and 904 cm⁻¹, peak due to Sun-Wang resonance between the S-C \equiv N bending mode² and the overtone of the S-C \equiv N bending mode at 1013 cm⁻¹ and 1368 cm⁻¹,² C=N stretching mode at 1625 cm⁻¹,³ C \equiv N stretching modes at 2122 cm⁻¹ and 2180 cm⁻¹,⁴ a combination mode of C=N stretching and S-C \equiv N bending at 2563 cm⁻¹,⁵ combinational mode of Hg-C stretching, S-C \equiv N bending and C \equiv N stretching mode at 2847 cm⁻¹ and K-N stretching at 3427 cm⁻¹.³



Figure S2: Ambient FTIR Spectrum of KHg(CN)₂(SCN)

735 cm⁻¹: E. Elijošiute, O. Eicher-Lorka, E. Griškonis, I. Matulaitiene, D. Jankunaite and G. Denafas, "Molecular structure of mercury(II) thiocyanate complexes based on DFT calculations and experimental UV-electron spectroscopy and Raman Studies," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 115, pp. 574-582, 2013.

Y. Li, P. Wang, Z. Zhang, Y. Li, F. Ma and M. Sun, "Nonlinear resonances in electrochemical SERS of SCN–, rotation-resolved Raman and anti-Stokes Raman of SCN– in HV-TERS," *RSC Advances*, vol. 2, no. 32, pp. 12160-12163, 2012.

886 cm⁻¹ and **904** cm⁻¹: Y. Li, P. Wang, Z. Zhang, Y. Li, F. Ma and M. Sun, "Nonlinear resonances in electrochemical SERS of SCN–, rotation-resolved Raman and anti-Stokes Raman of SCN– in HV-TERS," *RSC Advances*, vol. 2, no. 32, pp. 12160-12163, 2012.

1013 cm⁻¹ and **1368** cm⁻¹: Y. Li, P. Wang, Z. Zhang, Y. Li, F. Ma and M. Sun, "Nonlinear resonances in electrochemical SERS of SCN–, rotation-resolved Raman and anti-Stokes Raman of SCN– in HV-TERS," *RSC Advances*, vol. 2, no. 32, pp. 12160-12163, 2012.

1625 cm⁻¹: C. Wang, L. Wang, L. Yu, H. Ren and Y. Lv, "Synthesis and application of new rhodamine 6G-derivative fluorescent probe molecules," *E3S Web of Conferences*, vol. 260, pp. 010091-010095, 2021.

2122 cm⁻¹ and 2180 cm⁻¹: S. Hibble, G. Wood, E. Bilbé, A. Pohl, M. Tucker, A. Hannon and A. Chippindale, "Structures and negative thermal expansion properties of the one-dimensional cyanides, CuCN, AgCN and AuCN," *Zeitschrift für Kristallographie - Crystalline Materials*, vol. 225, no. 11, pp. 457-462, 2010

2563 cm⁻¹: D. Adams and P. Hatton, "Spectroscopy at high pressures. Part 42.—The Raman spectrum of mercury(II) thiocyanate," *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics,* vol. 79, no. 5, pp. 695-705, 1983.

2847 cm⁻¹ and 3427 cm⁻¹: C. Wang, L. Wang, L. Yu, H. Ren and Y. Lv, "Synthesis and application of new rhodamine 6G-derivative fluorescent probe molecules," *E3S Web of Conferences*, vol. 260, pp. 010091-010095, 2021.

Powder X-ray diffraction (PXRD) of KHg(CN)₂(SCN)

Figure S3 represents the PXRD pattern along with corresponding (hkl) values measured for the material with wavelength of Cu K α = 1.54056 Å based on the single crystal diffraction data.



Figure S3: PXRD pattern of KHg(CN)₂(SCN) based on the single crystal diffraction data

Interatomic lengths and Bond angles of KHg(CN)₂(SCN)

The interatomic lengths of KHg(CN)₂(SCN) at ambient conditions are Hg-S= 3.144 Å, C1-N1= 1.136 Å, C-S= 1.644 (5) Å, C2-N2= 1.168 (7) Å, C1-N1= 1.136 (5) Å, Hg-C= 2.046 (4) Å, K-K= 4.2576 (3) Å and K-N= 3.068 (3) Å. The bond angles of KHg(CN)₂(SCN) at ambient conditions are represented in Table S1.

Number	Atom 1	Atom 2	Atom 3	Angle
				(°)
1	C1	Hg1	S1	91.4
2	C1	Hg1	C1	180.0
3	C1	Hg1	S1	91.4
4	C1	Hg1	S1	88.6
5	C1	Hg1	S1	88.6
6	S1	Hg1	C1	88.6

7	S1	Hg1	S1	85.24
8	S1	Hg1	S1	94.76
9	S1	Hg1	S1	180.00
10	C1	Hg1	S1	88.6
11	C1	Hg1	S1	91.4
12	C1	Hg1	S1	91.4
13	S1	Hg1	S1	180.00
14	S1	Hg1	S1	94.76
15	S1	Hg1	S1	85.24
16	C1	N1	K1	123.8
17	C1	N1	K1	123.8
18	K1	N1	K1	87.9
19	Hg1	C1	N1	179.9
20	Hg1	S1	C2	96.4
21	Hg1	S1	Hg1	85.24
22	Hg1	S1	Hg1	167.17
23	Hg1	S1	Hg1	93.33
24	C2	S1	Hg1	96.4
25	C2	S1	Hg1	96.4
26	C2	S1	Hg1	96.4
27	Hg1	S1	Hg1	93.33

28	Hg1	S1	Hg1	167.17
29	Hg1	S1	Hg1	85.24
30	C2	N2	K1	130.5
31	C2	N2	K1	130.5
32	S1	C2	N2	180.0

Table S1: Bond angles of KHg(CN)₂(SCN) at ambient conditions

Raman Spectra of KHg(CN)₂(SCN) below room temperature 80 K to 300 K

Figure S4 represents the Raman spectra of KHg(CN)₂(SCN) while warming from 100 K to 300 K. Analyzing the warming cycle (100 K - 300 K) (Figure 3, main manuscript), modes at 891 cm⁻¹, 896 cm⁻¹ and 903 cm⁻¹ corresponding to overtone of SCN bending mode show clear blue shift. On the other hand, the primary SCN bending mode at 443 cm⁻¹ showed anomaly in this warming cycle. Other modes such as C-S stretching modes (666 cm⁻¹, 722 cm⁻¹, 726 cm⁻¹, 733 cm⁻¹), Hg-S stretching (305 cm⁻¹) mode red shifted from 100 K -300 K. These changes are reversible in the cooling cycle (300 K-80 K) (Figure S8). The traced CN stretching mode (2184 cm⁻¹) blue shifted below 160 K while warming from 100 K to 300 K. Above 240 K, the high frequency shoulder mode of Hg-C Stretching (385 cm⁻¹) shows blue shift and CN stretching mode (2184 cm⁻¹) shows red shift. Considering the fact that the measurements do not have any kinetic impact and were conducted with equal sized temperature intervals, these aforementioned changes in d ω /dT at 160 K and 240 K, can be attributed to the order-disorder phase transition. Similar changes in the frequency variation with temperature for all the modes in cooling cycle (300 K - 80 K) are shown in Figure S8.







(c)

(d)



Figure S4: Raman Spectra of KHg(CN)₂(SCN) during warming cycle (100 K - 300 K)

Figure S5 represents the Raman spectra of $KHg(CN)_2(SCN)$ while lowering the temperature from 300 K to 80 K. It can be observed that 286 cm⁻¹ related to Hg-C-N bending mode shows increment in intensity as compared to that of Hg-S stretching mode at 305 cm⁻¹.











Figure S5: Raman Spectra of KHg(CN)₂(SCN) during cooling cycle (300 K - 80 K)

Raman Spectra of KHg(CN)₂(SCN) above room temperature (300 K - 400 K)

Figure S6 represents Raman spectra of $KHg(CN)_2(SCN)$ while heating above ambient temperature to 400 K. The intensity of 286 cm⁻¹ mode is less as compared to that of 305 cm⁻¹. By contrast the 286 cm⁻¹ mode intensifies as compared to the 305 cm⁻¹ mode while cooling back to ambient temperature (Figure S6(a)).

Figure 3, Main manuscript shows the variation of Raman shift of $KHg(CN)_2(SCN)$ when temperature is increased from 300 K to 400 K (heating cycle). When the material was heated above 300 K, the primary SCN mode (443 cm⁻¹) showed red shift while its overtone mode (891 cm⁻¹, 896 cm⁻¹, and 903 cm⁻¹) showed clear blue shift with increasing temperature. All other traced modes (286 cm⁻¹, 305 cm⁻¹, 362 cm⁻¹, 666 cm⁻¹, 722 cm⁻¹, 726 cm⁻¹, 733 cm⁻¹, 2130 cm⁻¹, and 2184 cm⁻¹) were observed to show red shift with an increase in temperature. It was observed that the high frequency shoulder of Hg-C stretching mode at ~ 385 cm⁻¹ shows blue shift above 240 K up to 340 K while CN stretching modes shows red shift throughout 160 K -400 K.





Figure S6: Raman Spectra of KHg(CN)₂(SCN) during heating cycle from ambient to
400 K for (a) HgC and HgS stretching related modes (b) CS stretching modes (c)
overtone of SCN bending modes and (d) CN stretching modes.

Figure S7 represents Raman spectra of $KHg(CN)_2(SCN)$ while cooling from 380 K to ambient one.





Figure S7: Raman Spectra of KHg(CN)₂(SCN) during cooling cycle from 380 K to ambient temperature.

It can be observed in Figure S8 that, the modes at 891 cm⁻¹, 896 cm⁻¹ and 903 cm⁻¹ corresponding to overtone of SCN bending show clear red shift on cooling down the material up to 80 K. Further, high frequency shoulder of Hg-C stretching also show red shift below 160 K in this temperature regime. Furthermore, CN stretching mode at 2184 cm⁻¹ was found to show significant red shift when cooled below 160 K. A primary SCN bending mode at 443 cm⁻¹ show an anomaly in this cooling cycle suggesting the probability of structural change for KHg(CN)₂(SCN) below room temperature. Rest all the traced modes related to Hg-C-N bending (286 cm⁻¹), Hg-S stretching (305 cm⁻¹), C-S stretching modes (666 cm⁻¹, 722 cm⁻¹, 726 cm⁻¹ and 733 cm⁻¹) and CN stretching modes (2130 cm⁻¹) shows blue shift on cooling down the sample from 300 K - 80 K.

Figure S8 represents Raman shift variation with temperature in cooling cycle (400 K - 300 K). A clear red shift was observed for overtone of SCN bending modes (891 cm⁻¹, 896 cm⁻¹, and 903 cm⁻¹) and high frequency shoulder of Hg-C stretching of 362 cm⁻¹. Primary SCN bending mode (443 cm⁻¹) shows anomaly. All other modes (286 cm⁻¹, 305 cm⁻¹, 362 cm⁻¹, 666 cm⁻¹, 722 cm⁻¹, 726 cm⁻¹, 733 cm⁻¹, 2130 cm⁻¹, and 2184 cm⁻¹) shows blue shift in this temperature range (400 K - 300 K).

While cooling back from 400 K - 300 K, the high frequency shoulder of Hg-C stretching mode shows red shift throughout with a kink between 340 K and 380 K and both CN stretching and C-S stretching mode ~ 666 cm⁻¹ show clear change below 340 cm⁻¹. A small change in $d\omega/dT$ around 340 K - 360 K can be observed for all the modes in heating cycle (300 K - 400 K) pointing towards the possibility of phase transition in this temperature range.









Raman Shift	Modes	dœ/dT	dω/dT	dœ/dT	dœ/dT	dœ/dT	Temperature
(cm ⁻¹)	Assignme	100 K -	160 K -	240 K - 300	300 K - 340	360 K - 100	at which a mode was
	nt	160 K -	240 K	240 K - 500 K	500 K - 540 K	500 K - 400 K	observed
286	Hg-C-N	-0 0	01	-0.008	-0.018	-0.014	Δ11
200	hending	-0.0	01	-0.000	-0.010	-0.014	temperatures
305	Hg-S	0.001 +	0.006 +	0.003 +	-0.013	0.0	Ambient
505	stretching	0.001 ±	$0.000 \pm$	0.003 ±	-0.015	0.0	onwards
	stretening	010	0.007	0.0150			onwards
443	S-C≡N	-	-	0.008 ± 0.003	-0.02915	-0.006	Ambient
	bending						onwards
362	Hg-C	-0.0	13	-0.018	0.003 ±	-0.034 ±	Ambient
	stretching				0.023	0.01	onwards
*385	Hg-C	0.001	-0.019	$0.049 \pm$	$0.104 \pm$	-0.031	Ambient
	stretching			0.091	0.050		onwards
666	C-S	0.001	-0.02	$-0.024 \pm$	-0.0132	$0.004 \pm$	Ambient
	stretching			0.004		0.009	onwards
722	C-S	-0.008 \pm	0.001	-0.02	-0.017	-0.050	Ambient
	stretching						onwards
726	C-S	-0.0	11	-0.01	-0.013	-0.008	Ambient
	stretching						onwards
733	C-S	-0.0	09	-0.01	-0.009	-0.008	Ambient
	stretching						onwards
891	Overtone	$0.017 \pm$	0.011 ±	0.017 ± 0.003	$0.019 \pm$	$0.028 \pm$	Ambient
	of S-C≡N				0.003	0.005	onwards
	bending	0.001	0.001				
896	Overtone	$0.020 \pm$	0.014±	0.014 ± 0.008	0.014 ±	0.041 ±	Ambient
	of S-C≡N	0.			0.004	0.012	onwards
		(d)			(e)		

Figure S8: Raman Shift as a function of temperature for KHg(CN)₂(SCN) during cooling cycle from 400 K to 80 K.

Table S2, describes the d ω /dT variation of the Raman modes during warming cycles (100 K -

300 K and 300 K - 400 K).

	bending	002	0.001				
903	Overtone	0.016 ±	0.014	0.013 ± 0.002	$0.017 \pm$	0.012 ±	Ambient
	of S-C≡N	0.003			0.005	0.009	onwards
	bending						
2130	C≡N	-0.025	-0.030	-0.031	-0.029	-0.032	Ambient
	stretching						onwards
2184	C≡N	7.11473E-	-0.011	-0.013	-0.012	-0.015	Ambient
	stretching	4					onwards

Table S2: Rate of change of frequency as a function of temperature (The error bars are rounded off to three decimal places only. Modes with error bars higher than the slope value itself have not been written above) (*) describes that the particular mode could not be traced using NUV Raman facility and was only discernible for all temperatures when recorded at UGC-DAE, Indore facility.

DSC Thermogram of KHg(CN)₂(SCN)



Figure S9: DSC Thermogram of KHg(CN)₂(SCN) measured from - 80 °C to + 130 °C

(193 K - 403 K)

DSC measurements shows presence of structural changes in $KHg(CN)_2(SCN)$ around 258 K which is close to the changes observed in the Raman data around 240 K.

High Temperature X-ray Diffraction (HTXRD) pattern of KHg(CN)₂(SCN)

Figure S10 shows the HTXRD pattern of KHg(CN)₂(SCN) up to 448 K. The material exhibits complete reversibility on decrement of temperature to the ambient.



Figure S10: HTXRD pattern of KHg(CN)₂(SCN)

Raman Spectra of CS stretching mode (~ 726 cm⁻¹, ~ 733 cm⁻¹, and ~ 740 cm⁻¹)

As shown in Figure S11, CS stretching mode at ~ 726 cm⁻¹, ~ 733 cm⁻¹, and ~ 740 cm⁻¹ shows a clear blue shift with an increase in pressure.



Figure S11: Raman Spectra of CS stretching mode (~ 726 cm⁻¹, ~ 733 cm⁻¹, and ~ 740

cm⁻¹)

Rate of change of Raman frequency as a function of pressure

Raman Shift	Modos Assignment	dω/dP	dω/dP	dω/dP	Pressure at which a
(cm ⁻¹)	would Assignment	0 GPa - 0.7 GPa	0.7 GPa - 3.0	3.0 GPa - 8.0	mode was observed
			GPa	GPa	
*158	Hg-SC bending	5.0 ± 3.2	6.8 ± 0.4	2.3 ± 0.6	0.2 GPa - 11.7 GPa
*210	Hg-S stretching	-	-	-	5.9 GPa - 9.3 GPa
*240	Hg-S stretching	6.0	-	-	0.2 GPa - 0.7 GPa
291	Hg-C-N bending	2.5 ± 0.6	-5.8	-0.6	Ambient onwards
311	Hg-S stretching	-4.1	-7.3	-2.7	Ambient onwards
*330	Hg-C stretching	-	-	1.0 ± 0.4	2.1 GPa - 9.3 GPa
368	Hg-C stretching	-2.5	-6.4	1.7	Ambient onwards
398	Hg-C stretching	-0.9	-2.8	4.3 ± 0.7	0.2 GPa - 7.2 GPa
451	S-C≡N bending	-	-15.4	-0.7	Ambient onwards
481	S-C≡N bending	-3.1	-3.6	-0.4	Ambient onwards
671	C-S stretching	-1.9	-9.4	-0.6	Ambient onwards
726	C-S stretching	4.4 ± 0.1	4.3 ± 0.4	3.2 ± 0.5	Ambient onwards
733	C-S stretching	3.2 ± 2.4	4.2 ± 0.1	3.0 ± 0.1	Ambient onwards
740	C-S stretching	3.2 ± 2.4	4.3	3.2	Ambient onwards
898	Overtone of S-C≡N bending	-6.0	-5.4	-1.2	Ambient onwards
903	Overtone of S-C≡N bending	-1.1	-5.6	-1.1	Ambient onwards
910	Overtone of S-C≡N bending	-2.5	-3.7	-0.8	Ambient onwards
2134	C≡N stretching	10.0 ± 0.1	8.5 ± 0.6	3.0±0.1	Ambient onwards
2189	C≡N stretching	3.0 ± 0.2	3.6 ± 0.2	4.0 ± 0.1	Ambient onwards

Table S3: Rate of change of frequency as a function of temperature (The error bars are rounded off to one decimal place only. Modes with error bars higher than the slope value itself have not been written above) (*) describes the modes could be traced as a function of pressure only.

Le-Bail Refinement plots of KHg(CN)₂(SCN) from High Temperature X-ray Diffraction

(HTXRD) measurements at various temperatures





(c)

(d)



(e)

Figure S12: Le-Bail Refinement plots of KHg(CN)₂(SCN) from High Temperature Xray Diffraction (HTXRD) measurements at (a) 323 K (b) 348 K (c) 373 K (d) 398 K and (e) 423 K

Determination of Bulk Modulus of KHg(CN)₂(SCN) in orthorhombic and monoclinic phase using HPXRD and DFT data.

The pressure- volume data within monoclinic phase transition state (4.6 GPa – 13.2 GPa) in HPXRD data were fitted using third order Birch- Murnaghan equation of state in EOSFit Software. The data file consisting of volumes along with their errors and the pressure values was prepared and loaded into EOSFit software. Further, third order Birch- Murnaghan (BM) equation of state

$$P = \frac{3K_0}{2} \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} (K' - 4) \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\}$$

where K_0 and K' are the isothermal bulk modulus and its pressure derivative respectively. V_0 and V describe the volume at ambient condition and at various pressures respectively.⁶ was fitted to obtain the isothermal Bulk modulus and its first pressure derivative. The isothermal Bulk modulus (K₀) and its pressure derivative (K') was found to be 12.4 ± 0.9 GPa and 2.6 ± 0.1 GPa. Thus, obtained low values of bulk modulus indicate high compressibility as seen in the volume compression in monoclinic phase in HPXRD data (Figure S13(a)). Similarly, the isothermal Bulk modulus (K₀) and its first derivative (K') for orthorhombic phase (0 GPa - 15.4 GPa) in DFT data was found to be 14.5 ± 0.2 GPa and 4.3 ± 0.1 GPa respectively (Figure S13(b)).



Figure S13: (a) BM fit for HPXRD data (b) BM fit of DFT data

The Γ-point frequency of phonon modes based on DFT calculations

The Γ -point frequencies based on DFT calculations are tabulated below.

IR active modes and	Raman active modes	Hyper-Raman active
their frequency	and their frequency	modes and their
		frequency

Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency
	(cm ⁻¹)		(cm ⁻¹)		(cm ⁻¹)
B _{1u}	23.207	B _{3g}	17.203	B _{1u}	23.207
B _{1u}	29.096	B _{1g}	51.895	A _u	25.923
B _{3u}	37.275	B _{2g}	55.803	B _{1u}	29.096
B _{1u}	48.672	B _{1g}	61.826	B _{3u}	37.275
B _{2u}	52.692	Ag	65.85	B _{1u}	48.672
B _{3u}	64.871	B _{3g}	70.357	B _{2u}	52.692
B _{2u}	83.932	B_{1g}	97.167	B _{3u}	64.871
B _{3u}	87.391	Ag	113.755	A _u	71.732
B _{1u}	88.238	Ag	122.164	B _{2u}	83.932
B _{1u}	111.181	B _{3g}	125.52	B _{3u}	87.391
B _{2u}	126.351	B _{3g}	129.329	B _{1u}	88.238
B _{2u}	133.548	B _{1g}	149.134	B _{1u}	111.181
B _{3u}	148.362	B _{2g}	269.04	B _{2u}	126.351
B _{3u}	328.839	B _{1g}	269.861	B _{2u}	133.548
B _{1u}	333.318	B _{3g}	278.025	B _{3u}	148.362
B _{2u}	340.563	Ag	282.57	B _{3u}	328.839
B _{1u}	413.948	B _{3g}	379.336	A _u	330.015
B _{2u}	416.908	Ag	382.080	B _{1u}	333.318
B _{1u}	449.422	B _{3g}	448.078	B _{2u}	340.563
B _{3u}	452.253	B _{1g}	452.177	B _{1u}	413.948
B _{2u}	755.811	Ag	756.868	B _{2u}	416.908
B _{2u}	2125.032	Ag	2130.618	B _{1u}	449.422

B _{1u}	2215.031	B _{3g}	2216.049	B _{3u}	452.253
B _{2u}	2215.599	Ag	2216.895	B _{2u}	755.811
				B _{2u}	2125.032
				B_{1u}	2215.031
				B _{2u}	2215.599

Table S4: Γ-point frequencies of phonon modes based on DFT calculations

References

- E. Elijosiute, O. Eicher-Lorka, E. Griskonis, I. Matulaitiene, D. Jankunaite and G. Denafas, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2013, 115, 574-582.
- 2. Y. Li, P. Wang, Z. Zhang, Y. Li, F. Ma and M. Sun, RSC Adv., 2012, 2, 12160-12163.
- C. Wang, L. Wang, L. Yu, H. Ren and Y. Lv, *E3S Web Conf.*, 2021, 260, 010091-010095.
- S. Hibble, G. Wood, E. Bilbe, A. Pohl, M. Tucker, A. Hannon and A. Chippindale, Z. Kristallogr. Cryst. Mater., 2010, 225, 457-462.
- 5. D. Adams and P. Hatton, J. Chem. Soc., Faraday Trans., 1983, 79, 695-705.
- 6. A. Dewaele, P. Loubeyre and M. Mezouar, *Phys. Rev. B.*, 2004, **70**, 0941121-0941128.