

Supporting information for

Long-Lived Electronic Coherence of Iodine in the
Condensed Phase: Sharp Zero-Phonon Lines in the
 $B \leftrightarrow X$ Absorption and Emission of I_2 in Solid Xe

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Table S1. Positions and linewidths of vibronic ZPLs and PSBs in absorption spectrum of I₂/Xe (T = 10 K). Positions and linewidths are obtained from combined least-squares fits of ZPLs (Lorentzian function) and PSBs (Gaussian function). All values are in units of cm⁻¹. Fit uncertainties are indicated in the brackets.

B←X	ZPL position	PSB position	ZPL width	PSB width
8'← 0''	16080 (7)			
9'← 0''	16188 (7)			
10'← 0''	16290 (6)	16288 (>10)	6 (5)	79 (>10)
11'← 0''	16394 (3)	16414 (9)	9 (4)	64 (>10)
12'← 0''	16496.1 (0.9)	16525 (5)	15 (2)	53 (>10)
13'← 0''	16597.5 (0.8)	16620 (5)	14 (2)	56 (9)
14'← 0''	16697.2 (0.4)	16728.5 (0.9)	15.9 (1.3)	42 (3)
15'← 0''	16795.3 (0.4)	16824.8 (0.9)	17.1 (1.2)	40 (2)
16'← 0''	16892.1 (0.4)	16922.8 (0.7)	17.6 (1.1)	36.7 (1.4)
17'← 0''	16987.2 (0.4)	17017.6 (0.5)	18.6 (0.9)	37.0 (1.0)
18'← 0''	17080.2 (0.3)	17111.8 (0.4)	17.9 (0.6)	37.7 (0.9)
19'← 0''	17171.9 (0.2)	17203.5 (0.4)	18.5 (0.8)	36.3 (1.0)
20'← 0''	17261.5 (0.3)	17293.3 (0.4)	18.7 (0.8)	35.1 (1.0)
21'← 0''	17349.3 (0.3)	17381.7 (0.3)	18.4 (0.7)	32.8 (0.7)
22'← 0''	17435.1 (0.2)	17467.3 (0.3)	18.2 (0.7)	32.4 (0.7)
23'← 0''	17518.4 (0.2)	17551.3 (0.3)	20.9 (1.0)	29.9 (0.8)
24'← 0''	17600.3 (0.3)	17633.2 (0.3)	18.9 (0.9)	29.4 (0.7)
25'← 0''	17679.6 (0.2)	17713.2 (0.3)	20.1 (1.0)	28.4 (0.8)
26'← 0''	17756.9 (0.3)	17791.3 (0.3)	18.4 (1.1)	25.5 (1.0)
27'← 0''	17832.3 (0.3)	17866.8 (0.4)	19 (2)	24.8 (1.5)
28'← 0''	17905.2 (0.3)	17941.4 (0.5)	17 (2)	23 (2)
29'← 0''	17976.8 (0.5)	18012.2 (0.7)	22 (3)	25 (3)
30'← 0''	18046.8 (0.6)	18081.7 (1.0)	16 (4)	20 (4)
31'← 0''	18114.2 (0.9)	18148.6 (1.2)	29 (4)	26 (4)

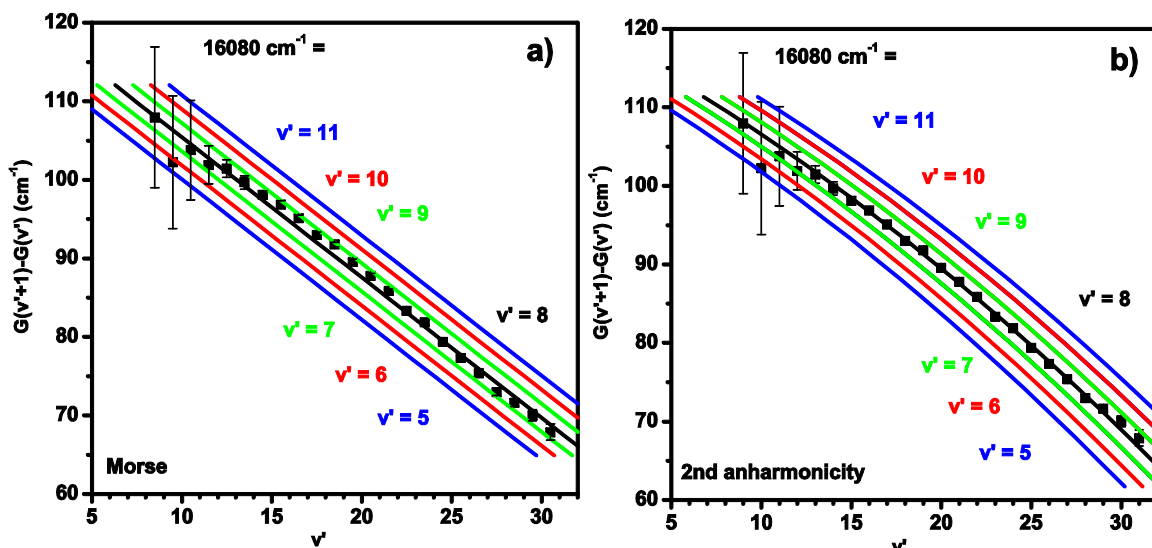


Figure S1. Birge-Sponer plots obtained from ZPL positions listed in Table S1 with different B-state vibrational numberings. a) Least-squares linear fits to experimental energy differences $G(v'+1)-G(v')$ with Morse function ($G(v) = \omega_e(v+0.5) - \omega_e x_e(v+0.5)^2$). b) Least-squares fits (2nd order polynomial) to experimental energy differences with term value function including 2nd anharmonicity ($G(v) = \omega_e(v+0.5) - \omega_e x_e(v+0.5)^2 + \omega_e y_e(v+0.5)^3$). Different ZPL numberings in both panels are indicated with the color coded numbering of the lowest energy ZPL in absorption (16080 cm^{-1}). Note that the experimental energy differences (black dots) are only shown for numbering where 16080 cm^{-1} ZPL is assigned as $8' \leftarrow 0''$ B $\leftarrow$ X transition (black lines). Error bars for the experimental points originate from the fit errors in the ZPL positions in Table S1. For other numberings the points have been omitted for clarity, and only the fits are shown. Morse function (linear fit) describes the experimental points with reasonable accuracy, but for more precise description of the B-state potential at least second anharmonicity is necessary, as shown in the panel b). Variance of spectroscopic parameters obtained from the plots with different numberings is represented in Table S2.

Table S2. Spectroscopic parameters for the B-state in solid Xe with different vibrational numberings obtained from fits in Figure S1. Column v' indicates the assignment of the terminal B-state vibrational state for 16080 cm^{-1} ZPL in $B \leftarrow X$ transition. Based on the A-state behavior in solid Xe, ΔT_e value of -507 cm^{-1} is expected for the B-state (see ref. 20, main article). Our MD simulated B-state potential (see Table 1, main article) suggests significant reduction (-3.5 cm^{-1}) of the harmonic frequency in solid Xe. Vibrational numbering ($16080 \text{ cm}^{-1} = 8' \leftarrow 0''$) used in the main article is highlighted in boldface. All spectroscopic parameters are in units of cm^{-1} .

Morse: $G(v) = \omega_e(v+0.5) - \omega_e x_e(v+0.5)^2$

v'	ω_e (^d err.)	^a $\Delta\omega_e$ (^b $\Delta\omega_e$)	$\omega_e x_e$ (^d err.)	^a $\Delta\omega_e x_e$ (^b $\Delta\omega_e x_e$)	$\omega_e y_e$ (^d err.)	^a $\Delta\omega_e y_e$ (^b $\Delta\omega_e y_e$)	^c T_e (^e std.)	^a ΔT_e (^b ΔT_e)
11	128.6 (1.0)	+2.9 (+3.3)	0.89 (0.02)	+0.13 (+0.19)			14830 (9)	-940 (-940)
10	126.9 (0.9)	+1.2 (+1.6)	0.89 (0.02)	+0.13 (+0.19)			14960 (9)	-810 (-810)
9	125.1 (0.9)	-0.6 (-0.2)	0.89 (0.02)	+0.13 (+0.19)			15090 (9)	-680 (-680)
8	123.3 (0.9)	-2.4 (-2.0)	0.89 (0.02)	+0.13 (+0.19)			15210 (9)	-560 (-560)
7	121.5 (0.8)	-4.2 (-3.8)	0.89 (0.02)	+0.13 (+0.19)			15330 (9)	-440 (-440)
6	119.7 (0.8)	-6.0 (-5.6)	0.89 (0.02)	+0.13 (+0.19)			15460 (9)	-310 (-310)
5	117.9 (0.8)	-7.8 (-7.4)	0.89 (0.02)	+0.13 (+0.19)			15570 (9)	-200 (-200)

2nd anharmonicity: $G(v) = \omega_e(v+0.5) - \omega_e x_e(v+0.5)^2 + \omega_e y_e(v+0.5)^3$

v'	ω_e (^d err.)	^a $\Delta\omega_e$ (^b $\Delta\omega_e$)	$\omega_e x_e$ (^d err.)	^a $\Delta\omega_e x_e$ (^b $\Delta\omega_e x_e$)	$\omega_e y_e$ (^d err.)	^a $\Delta\omega_e y_e$ (^b $\Delta\omega_e y_e$)	^b T_e (^e std.)	^a ΔT_e (^b ΔT_e)
11	123.7 (3.0)	-2.0 (-1.6)	0.55 (0.12)	-0.21 (-0.15)	-0.006 (0.002)	- (0)	14840 (3)	-930 (-930)
10	122.5 (2.7)	-3.2 (-2.8)	0.56 (0.11)	-0.20 (-0.14)	-0.006 (0.002)	- (0)	14960 (3)	-810 (-810)
9	121.4 (2.5)	-4.3 (-3.9)	0.58 (0.11)	-0.18 (-0.12)	-0.006 (0.002)	- (0)	15080 (3)	-690 (-690)
8	120.2 (2.3)	-5.5 (-5.1)	0.60 (0.11)	-0.16 (-0.10)	-0.006 (0.002)	- (0)	15200 (3)	-570 (-570)
7	119.0 (2.1)	-6.7 (-6.3)	0.61 (0.10)	-0.15 (-0.09)	-0.006 (0.002)	- (0)	15320 (3)	-450 (-450)
6	117.8 (1.9)	-7.9 (-7.5)	0.63 (0.10)	-0.13 (-0.07)	-0.006 (0.002)	- (0)	15440 (3)	-330 (-330)
5	116.5 (1.7)	-9.2 (-8.2)	0.65 (0.09)	-0.11 (-0.05)	-0.006 (0.002)	- (0)	15560 (3)	-210 (-210)

- Calculated using gas phase values from ref. 21 of the main article.
- Calculated using gas phase values from ref. 2 of the main article.
- Calculated average from all experimental transition energies in Table S1, using zero point energy of 104.96 cm^{-1} for the ground vibrational state ($E(0'')$), and the respective spectroscopic parameters.
- Least-squares fit uncertainty.
- Standard deviation from the average T_e value.

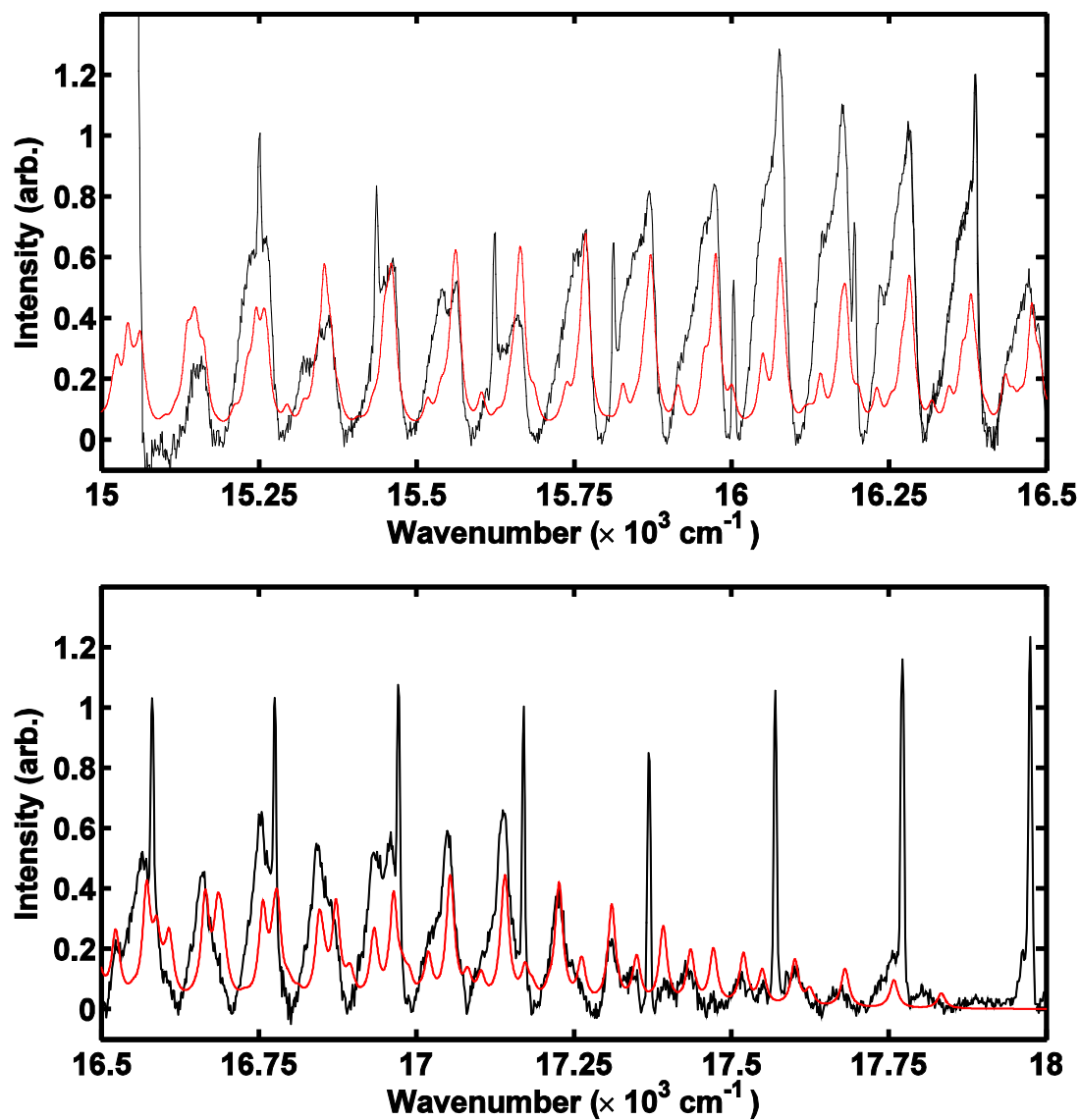


Figure S2. Enlargement of Figure 3c. of the main article. (black spectrum) baseline corrected experimental hot luminescence spectrum. (red spectrum) simulated spectrum. Note the sharp resonance Raman lines with (ca. 200 cm^{-1} spacing).

Table S3. Positions and relative intensities of identified hot luminescence B→X ZPLs. Measured from I₂/Xe sample at T = 10 K with 532 nm excitation. Transitions are listed in energetically ascending order (from left panel to right panel). The values are obtained from the spectral simulation described in the main text. The position values are in units of cm⁻¹ and the intensity values (Franck-Condon factors) are given normalized (Intensity = 1) to the 0'→15'' transition (12165 cm⁻¹). Horizontal lines separate approximately different hot luminescence structures in the emission spectrum. Note that transitions energies are only given for ZPLs located in emission structures without clearly overlapping Raman line (see Figure S2 above).

B→X	ZPL position	Intensity	B→X	ZPL position	Intensity
7'→4''	15136	0.61	22'→2''	17019	0.27
9'→5''	15150	0.54	20'→1''	17053	0.67
13'→7''	15164	0.32	23'→2''	17103	0.18
9'→4''	15354	0.78	22'→1''	17227	0.69
19'→8''	15539	0.18	20'→0''	17262	0.22
9'→3''	15558	0.56	23'→1''	17310	0.68
15'→6''	15563	0.39	21'→0''	17350	0.26
11'→4''	15565	0.61	24'→1''	17392	0.66
11'→3''	15770	0.75	22'→0''	17436	0.30
13'→4''	15770	0.25	25'→1''	17472	0.62
18'→5''	16050	0.40	23'→0''	17519	0.34
14'→3''	16075	0.63	26'→1''	17549	0.57
12'→2''	16080	0.53	24'→0''	17601	0.38
16'→3''	16271	0.35	27'→1''	17625	0.52
14'→2''	16282	0.69	25'→0''	17681	0.42
16'→2''	16477	0.74	26'→0''	17758	0.45
18'→2''	16665	0.65	27'→0''	17834	0.48
16'→1''	16684	0.45			
23'→4''	16692	0.36			
20'→2''	16846	0.47			
25'→4''	16853	0.25			
18'→1''	16873	0.58			