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

Laser Spectroscopic Characterization of Supersonic Jet Cooled 2,7-Diazaindole (27DAI)

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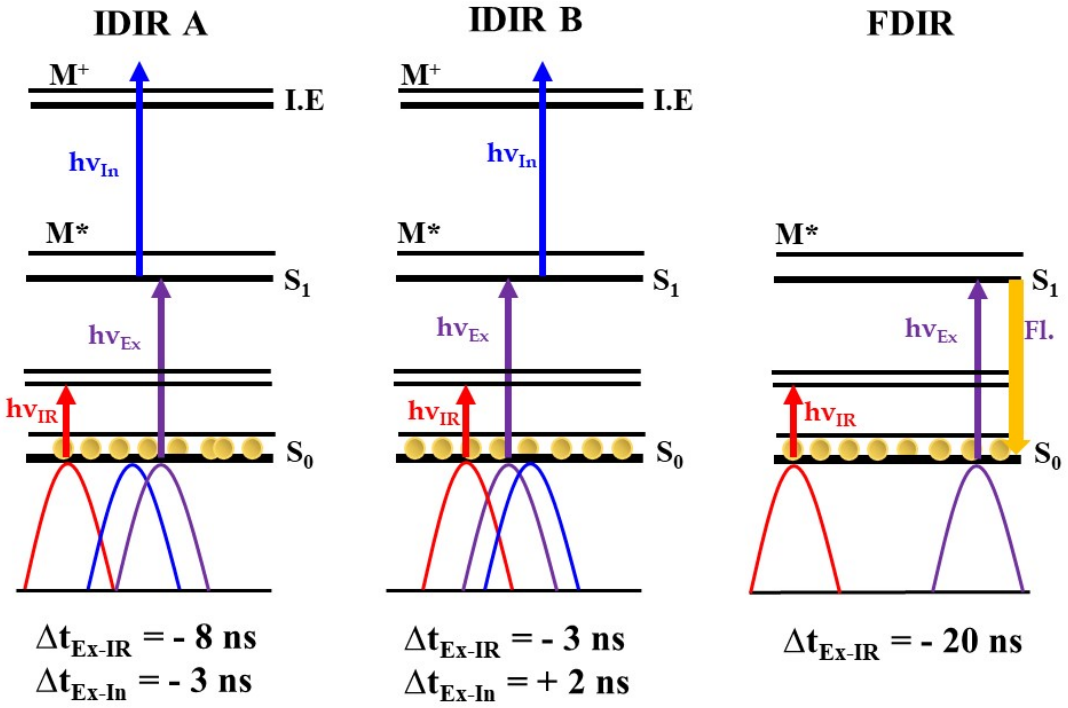

Scheme S1. Schematic representation of the laser delays showing IR laser interaction with the molecular beam (IDIR A) 8ns before the excitation (Ex) laser i.e., $\Delta t_{Ex\text{-}IR}$ = -8 ns, (IDIR B) 3 ns before the excitation (Ex) laser i.e., $\Delta t_{Ex\text{-}IR}$ = -3 ns and (FDIR) 20 ns before the excitation (Ex) laser i.e., $\Delta t_{Ex\text{-}IR}$ = -20 ns. The ionization laser pulses for IDIR techniques are also shown.

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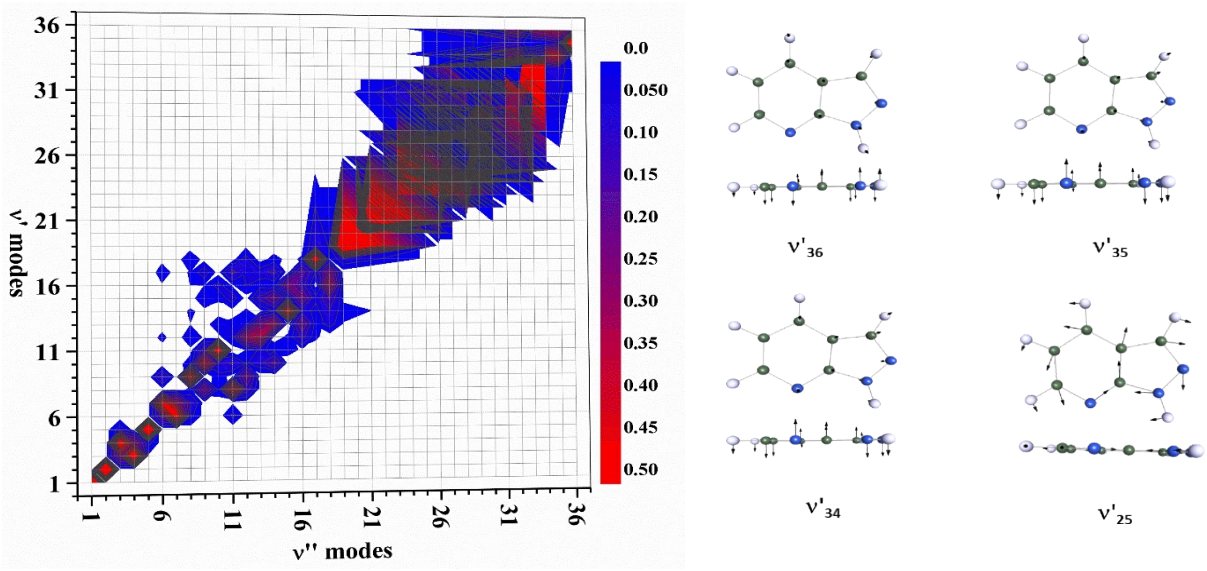

Figure S1. Duschinsky matrix of vibrational frequencies (ν'' in S_0 and ν' in S_1) of 2,7-diazaindole

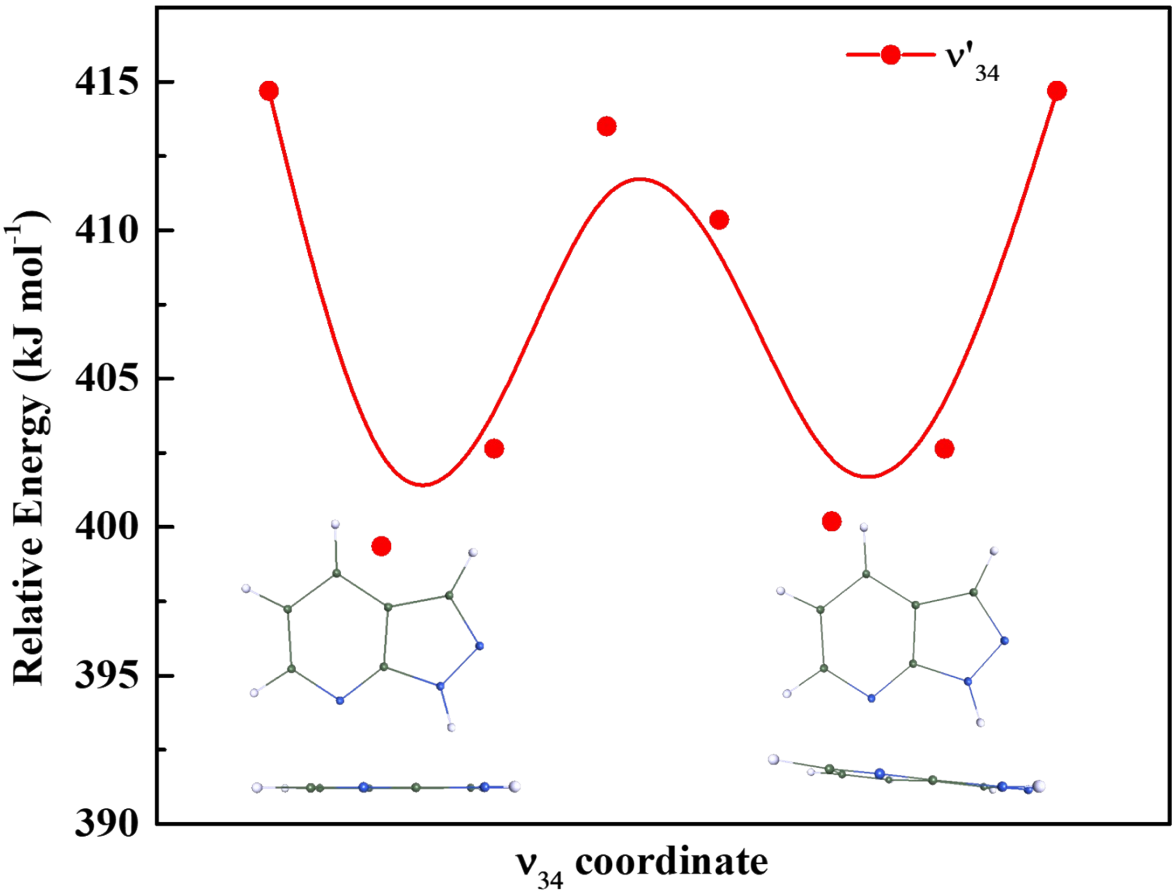

Figure S2. Potential surface showing a double minima for ν'_{34} mode in the R2PI spectra of 2,7-diazaindole.

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Table S1: Calculated vibrational frequencies in cm^{-1} of 27DAI molecule at three different methods.

Mode	B3LYP/def-SVP				B3LYP-D4/def2-TZVPP				ADC(2)(MP2)/cc-pVDZ			
	Symmetry (S_0)	S_0	Symmetry (S_1)	S_1	Symmetry (S_0)	S_0	Symmetry (S_1)	S_1	Symmetry (S_0)	S_0	Symmetry (S_1)	S_1
ν_{36}	a"	225	a"	133	a"	218	a"	169	a"	227	a"	242
ν_{35}	a"	258	a"	184	a"	252	a"	210	a"	258	a"	287
ν_{34}	a"	446	a"	316	a"	436	a"	318	a"	434	a"	456
ν_{33}	a"	556	a"	380	a"	490	a"	385	a"	536	a"	541
ν_{32}	a"	598	a"	542	a"	596	a"	539	a"	597	a"	603
ν_{31}	a"	683	a"	551	a"	677	a"	575	a"	688	a"	693
ν_{30}	a"	801	a"	637	a"	797	a"	644	a"	760	a"	749
ν_{29}	a"	813	a"	723	a"	810	a"	732	a"	815	a"	783
ν_{28}	a"	874	a"	792	a"	874	a"	780	a"	843	a"	837
ν_{27}	a"	971	a"	842	a"	969	a"	857	a"	950	a"	899
ν_{26}	a"	1006	a"	951	a"	997	a"	940	a"	979	a"	951
ν_{25}	a'	434	a'	409	a'	431	a'	409	a'	407	a'	433
ν_{24}	a'	554	a'	513	a'	560	a'	520	a'	540	a'	540
ν_{23}	a'	649	a'	636	a'	652	a'	634	a'	637	a'	629
ν_{22}	a'	785	a'	754	a'	785	a'	753	a'	780	a'	760
ν_{21}	a'	917	a'	891	a'	925	a'	898	a'	907	a'	900
ν_{20}	a'	947	a'	936	a'	951	a'	936	a'	932	a'	921
ν_{19}	a'	1052	a'	1031	a'	1054	a'	1029	a'	1057	a'	1003
ν_{18}	a'	1127	a'	1064	a'	1102	a'	1047	a'	1121	a'	1027
ν_{17}	a'	1130	a'	1111	a'	1142	a'	1067	a'	1136	a'	1082
ν_{16}	a'	1228	a'	1121	a'	1234	a'	1129	a'	1217	a'	1194
ν_{15}	a'	1257	a'	1188	a'	1264	a'	1200	a'	1243	a'	1205
ν_{14}	a'	1322	a'	1226	a'	1319	a'	1228	a'	1322	a'	1265
ν_{13}	a'	1339	a'	1257	a'	1332	a'	1253	a'	1346	a'	1270
ν_{12}	a'	1374	a'	1302	a'	1357	a'	1304	a'	1380	a'	1336
ν_{11}	a'	1415	a'	1367	a'	1407	a'	1368	a'	1456	a'	1387
ν_{10}	a'	1449	a'	1409	a'	1441	a'	1395	a'	1475	a'	1433
ν_{9}	a'	1506	a'	1437	a'	1497	a'	1440	a'	1502	a'	1448

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ν_8	a'	**1546**	a'	**1500**	a'	**1540**	a'	**1488**	a'	**1556**	a'	**1475**
ν_7	a'	**1633**	a'	**1615**	a'	**1618**	a'	**1563**	a'	**1645**	a'	**1586**
ν_6	a'	**1666**	a'	**1647**	a'	**1647**	a'	**1620**	a'	**1682**	a'	**1644**
ν_5	a'	**3150**	a'	**3164**	a'	**3159**	a'	**3177**	a'	**3240**	a'	**3220**
ν_4	a'	**3182**	a'	**3185**	a'	**3182**	a'	**3194**	a'	**3281**	a'	**3245**
ν_3	a'	**3201**	a'	**3237**	a'	**3202**	a'	**3237**	a'	**3318**	a'	**3261**
ν_2	a'	**3232**	a'	**3241**	a'	**3238**	a'	**3246**	a'	**3325**	a'	**3264**
ν_1	a'	**3645**	a'	**3557**	a'	**3662**	a'	**3577**	a'	**3764**	a'	**3572**

Table S2: Ground state geometries of 27DAI molecule at three different methods.

B3LYP/def-SVP				**B3LYP-D4/def2-TZVPP**				**ADC(2)(MP2)/cc-pVDZ**			
	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	-1.8986	-0.5241	0	C	1.9086	0.8004	0	C	-1.8988	-0.5262	0
C	-1.8192	0.8906	0	N	2.577	-0.3341	0	C	-1.8225	0.8954	0
N	-0.6827	1.581	0	N	1.6546	-1.3251	0	N	-0.6824	1.6037	0
C	0.4186	0.829	0	C	0.3838	-0.8428	0	C	0.417	0.8253	0
N	1.7143	1.2612	0	C	0.5036	0.5675	0	N	1.7159	1.2611	0
N	2.5965	0.2412	0	C	-0.6808	1.307	0	N	2.6107	0.2541	0
C	1.8894	-0.8746	0	C	-1.8664	0.5963	0	C	1.8871	-0.8814	0
C	0.4855	-0.5929	0	C	-1.8474	-0.8113	0	C	0.4879	-0.5995	0
C	-0.7365	-1.2881	0	N	-0.7439	-1.5488	0	C	-0.7396	-1.3017	0
H	-2.881	-1.0012	0	H	2.4415	1.7372	0	H	-2.8851	-1.0001	0
H	-2.7448	1.4784	0	H	1.9467	-2.2862	0	H	-2.7481	1.4833	0
H	2.3951	-1.8405	0	H	-0.6751	2.3889	0	H	2.4022	-1.8418	0
H	-0.7756	-2.3807	0	H	-2.8183	1.108	0	H	-0.7818	-2.396	0
H	2.0391	2.2209	0	H	-2.7839	-1.357	0	H	2.0374	2.2238	0

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Table S3: Excited state geometries of 27DAI molecule at three different methods.

B3LYP/def-SVP				B3LYP-D4/def2-TZVPP				ADC(2)(MP2)/cc-pVDZ			
	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.9099	-0.5093	0	C	-1.9058	-0.4959	0	C	-0.56	-1.8895	0
C	-1.8336	0.8812	0	C	-1.829	0.88	0	C	0.8458	-1.8771	0
N	-0.6604	1.6196	0	N	-0.6438	1.6131	0	N	1.6271	-0.705	0
C	0.3887	0.7992	0	C	0.3983	0.7978	0	C	0.8344	0.3657	0
N	1.7487	1.2394	0	N	1.7471	1.2279	0	N	1.2975	1.6678	0
N	2.6458	0.2827	0	N	2.6406	0.2672	0	N	0.3216	2.6786	0
C	1.8939	-0.8607	0	C	1.8669	-0.8742	0	C	-0.8143	1.9363	0
C	0.4678	-0.5833	0	C	0.4678	-0.5846	0	C	-0.5906	0.5113	0
C	-0.7484	-1.3374	0	C	-0.7473	-1.3201	0	C	-1.3623	-0.6911	0
H	-2.901	-0.9709	0	H	-2.8862	-0.953	0	H	-1.0646	-2.8626	0
H	-2.7564	1.4698	0	H	-2.7332	1.4731	0	H	1.407	-2.8163	0
H	2.4081	-1.8228	0	H	2.3672	-1.8293	0	H	2.2859	1.9348	0
H	-0.7869	-2.4248	0	H	-0.7911	-2.3963	0	H	-1.7727	2.4613	0
H	2.0437	2.2171	0	H	2.0486	2.1943	0	H	-2.4547	-0.714	0

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