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

Intermolecular dynamics of NH_3-rare gas complexes in the ν_2 umbrella region of NH_3 investigated by rovibrational laser jet-cooled spectroscopy and *ab initio* calculations

Y. Belkhodja, J. Loreau, A. van der Avoird, Y. Berger and P. Asselin

Supplementary material

Table S1: List of observed and *ab initio* frequencies (cm^{-1}) of both $\Pi_{e/f}(j=1,k=0)\leftarrow\Sigma_f(j=1,k=0)$ and $\Sigma_f(j=1,k=0)\leftarrow\Sigma_f(j=0,k=0)$ transitions for the four ortho NH_3-Rg complexes. The experimental frequency values in bold are derived from the spectral simulations.

	NH_3-Ne		NH_3-Ar		NH_3-Kr		NH_3-Xe	
			$\Pi_{e/f}(j=1,k=0)\leftarrow\Sigma_f(j=1,k=0)$					
Transition	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*
P(2)	949.71	949.989	949.998	949.949	951.241	950.778	954.069	952.694
P(3)	949.414	949.694	949.793	949.747	951.076	950.615	**953.919**	952.551
P(4)	949.104	949.385	949.583	949.54	950.905	950.448	953.762	952.401
P(5)	948.78	949.062	949.366	949.328	950.729	950.277	**953.595**	952.246
P(6)	948.443	948.729	949.144	949.11	950.548	950.1	**953.422**	952.086
P(7)	948.096	948.382	948.916	948.888	950.362	949.92	**953.241**	951.921
P(8)	-	948.027	948.682	948.66	950.171	949.735	**953.053**	951.75
P(9)	-	-	948.443	-	949.976	-	-	
P(10)	-	-	948.199	-	949.776	-	-	
P(11)	-	-	947.95	-	949.571	-	-	
P(12)	-	-	947.696	-	949.362	-	-	
P(13)	-	-	947.437	-	949.149	-	-	
P(14)	-	-	947.175	-	948.932	-	-	
P(15)	-	-	-	-	948.711	-	-	
Q(1)	950.257	950.537	**950.388**	950.336	951.555	951.089	954.346	952.964
Q(2)	950.262	950.542	**950.387**	950.336	951.553	951.087	954.343	952.961
Q(3)	950.27	950.55	950.386	950.336	951.551	951.086	954.337	952.957
Q(4)	950.28	950.561	950.385	950.336	951.547	951.083	954.331	952.952
Q(5)	950.293	950.574	950.384	950.337	951.542	951.08	954.322	952.946
Q(6)	950.308	950.591	950.382	950.337	951.536	951.077	954.311	952.939
Q(7)	950.327	950.61	950.38	950.339	951.53	951.073	954.299	952.93
Q(8)	950.349	950.634	950.378	950.339	951.523	951.068	954.285	952.92
Q(9)	950.374	-	950.376	-	951.514	-	954.269	-
Q(10)	950.404	-	950.373	-	951.505	-	954.252	-
Q(11)	950.437	-	950.371	-	951.495	-	954.233	-
Q(12)	950.475	-	950.368	-	951.484	-	954.212	-
Q(13)	950.518	-	950.366	-	951.472	-	954.19	-
Q(14)	950.623	-	950.363	-	951.46	-	954.165	-
Q(15)	950.257	-	950.361	-	951.447	-	954.139	-
Q(16)	-	-	950.359	-	951.432	-	954.112	-
Q(17)	-	-	950.357	-	951.418	-	954.083	-

Q(18)	-	-	950.355	-	951.402	-	954.052	-
Q(19)	-	-	950.354	-	951.386	-	954.019	-
Q(20)	-	-	950.353	-	951.369	-	953.984	-
Q(21)	-	-	950.353	-	951.352	-	953.948	-
Q(22)	-	-	-	-	951.334	-	953.911	-
Q(23)	-	-	-	-	951.315	-	953.872	-
Q(24)	-	-	-	-	951.296	-	953.831	-
Q(25)	-	-	-	-	951.277	-	955.519	-
Q(26)	-	-	-	-	951.238	-	-	-
Q(27)	-	-	-	-	951.217	-	-	-
Q(28)	-	-	-	-	951.555	-	-	-
R(0)	950.503	950.783	950.573	950.521	951.706	951.238	954.476	953.092
R(1)	950.734	951.015	950.752	950.7	951.85	951.381	954.596	953.213
R(2)	950.949	951.231	950.925	950.873	951.988	951.52	954.709	953.329
R(3)	951.148	951.431	951.091	951.041	952.122	951.654	954.815	953.439
R(4)	951.33	951.615	951.251	951.203	952.25	951.783	954.914	953.543
R(5)	951.496	951.782	951.404	951.359	952.372	951.908	955.006	953.642
R(6)	951.648	951.935	951.551	951.51	952.49	952.028	955.091	953.735
R(7)	**951.783**	952.072	951.691	951.654	952.602	952.142	955.17	953.823
R(8)	951.905	-	951.825	-	952.708	-	955.242	-
R(9)	952.012	-	951.952	-	952.81	-	955.309	-
R(10)	952.106	-	952.073	-	952.906	-	955.369	-
R(11)	952.187	-	952.188	-	952.997	-	955.424	-
R(12)	952.255	-	952.297	-	953.083	-	955.474	-
R(13)	952.31	-	952.399	-	953.164	-	955.519	-
R(14)	-	-	952.496	-	953.241	-	955.558	-
R(15)	-	-	952.586	-	953.312	-	955.593	-
R(16)	-	-	952.67	-	953.379	-	955.624	-
R(17)	-	-	952.749	-	953.441	-	955.65	-
R(18)	-	-	952.821	-	953.499	-	955.672	-
R(19)	-	-	952.888	-	953.552	-	955.689	-
R(20)	-	-	952.949	-	953.601	-	955.703	-
R(21)	-	-	953.005	-	953.645	-	955.713	-
R(22)	-	-	953.055	-	-	-	955.72	-
R(23)	-	-	953.1	-	-	-	955.723	-

	NH_3-Ne		NH_3-Ar		NH_3-Kr		NH_3-Xe	
	$\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$							
Transition	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*
P(1)	956.981	957.325	960.541	961.278	959.981	960.216	-	958.877
P(2)	956.723	957.065	960.353	961.089	959.829	960.065	-	958.748
P(3)	956.472	956.811	960.167	960.903	959.680	959.917	-	958.622
P(4)	956.227	956.562	959.984	960.719	959.534	959.771	-	958.500
P(5)	955.989	956.317	959.805	960.537	959.391	959.627	-	958.381
P(6)	955.756	956.078	959.629	960.358	959.252	959.486	-	958.265
P(7)	955.529	955.842	959.457	960.181	959.115	959.347	-	958.152
P(8)	955.306	955.610	959.287	960.006	958.981	959.211	-	958.043
P(9)	955.086	-	959.121	-	958.850	-	-	-
P(10)	954.869	-	958.957	-	958.722	-	-	-
P(11)	954.653	-	-	-	958.597	-	-	-
P(12)	954.436	-	-	-	958.474	-	-	-
P(13)	954.217	-	-	-	958.354	-	-	-
P(14)	-	-	-	-	958.236	-	-	-
P(15)	-	-	-	-	958.121	-	-	-
P(16)	-	-	-	-	958.009	-	-	-
P(17)	-	-	-	-	957.898	-	-	-
P(18)	-	-	-	-	957.791	-	-	-
R(0)	**957.516**	957.858	960.928	961.661	960.293	960.525	-	959.145
R(1)	**957.792**	958.132	961.126	961.856	960.454	960.683	-	959.285
R(2)	**958.073**	958.408	961.327	962.052	960.618	960.843	-	959.427
R(3)	**958.358**	958.686	961.530	962.251	960.784	961.005	-	959.573
R(4)	**958.645**	958.965	961.736	962.450	**960.953**	961.169	-	959.721
R(5)	**958.934**	959.243	961.945	962.652	**961.125**	961.336	-	959.873
R(6)	**959.223**	959.518	962.156	962.854	**961.299**	961.504	-	960.028
R(7)	**959.510**	959.789	962.368	963.058	**961.475**	961.674	-	960.185
R(8)	-	-	962.583	-	-	-	-	-
R(9)	-	-	962.799	-	-	-	-	-

Table S2 : List of observed $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ ortho transitions (cm^{-1}) for the three less abundant NH_3-Kr isotopomers with ^{82}Kr, ^{83}Kr and ^{86}Kr.

Transition	NH_3-^{82}Kr	NH_3-^{83}Kr	NH_3-^{86}Kr
	$\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=1,k=0)$		
P(1)	-	-	-
P(2)	-	-	-
P(3)	-	-	951.0779
P(4)	950.9024	-	950.9079
P(5)	950.7261	950.7281	950.7329
P(6)	950.5444	950.5468	950.5528
P(7)	950.3581	950.3606	950.3678
P(8)	950.1662	950.1689	950.1777
P(9)	949.9693	949.9735	-
P(10)	949.7685	949.7730	949.7840
P(11)	949.5628	949.5672	949.5801
P(12)	-	949.3577	949.3720
P(13)	-	949.1444	949.1602
P(14)	-	948.9270	948.9440
P(15)	-	-	-
P(16)	-	-	-
P(17)	-	-	-
P(18)	-	-	-
Q(1)	951.5557	951.5557	951.5557
Q(2)	951.5538	951.5538	951.5538
Q(3)	951.5510	951.5510	951.5510
Q(4)	951.5472	951.5472	951.5472
Q(5)	951.5424	951.5424	951.5424
Q(6)	951.5368	951.5368	951.5368
Q(7)	951.5304	951.5304	951.5304
Q(8)	951.5231	951.5231	951.5231
Q(9)	951.5147	951.5147	951.5147
Q(10)	951.5055	951.5055	951.5055
Q(11)	951.4955	951.4955	951.4955
Q(12)	951.4846	951.4846	951.4846
Q(13)	951.4729	951.4729	951.4729
Q(14)	951.4603	951.4603	951.4603
Q(15)	951.4470	951.4470	951.4470
Q(16)	951.4329	951.4329	951.4329
Q(17)	951.4181	951.4181	951.4181
Q(18)	951.4026	951.4026	951.4026
Q(19)	951.3865	951.3865	951.3865
Q(20)	951.3697	951.3697	951.3697
Q(21)	951.3524	951.3524	951.3524
Q(22)	951.3343	951.3343	951.3343
Q(23)	951.3157	951.3157	951.3157
Q(24)	951.2969	951.2969	951.2969
Q(25)	951.2774	951.2774	951.2774
Q(26)	951.2584	951. 2584	951.2584

Q(27)	951.2384	951.2384	951.2384
Q(28)	951.2177	951.2177	951.2177
R(2)	-	-	951.9873
R(3)	952.1244	-	952.1203
R(4)	952.2523	-	952.2479
R(5)	952.3756	-	952.3699
R(6)	952.4936	-	952.4869
R(7)	952.6057	952.6035	952.5985
R(8)	952.7127	-	952.7050
R(9)	952.8142	-	952.8060
R(10)	952.9107	-	952.9023
R(11)	953.0019	952.9996	952.9927
R(12)	953.0883	953.0862	953.0791
R(13)	953.1694	-	953.1598
R(14)	953.2461	-	953.2364
R(15)	953.3182	953.3153	953.3081
R(16)	953.3843	-	953.3745
R(17)	953.4470	-	953.4365
R(18)	953.5045	-	953.4946
R(19)	-	-	953.5482
R(20)	-	-	953.5965

Table S3: Spectroscopic constants (MHz) of the $\Pi_{e/f}(j=1,k=0)$ state of the three minor NH_3-Kr isotopomers derived from rovibrational band contour simulations. Molecular parameters are derived using the expressions of the pseudodiatomic model. Ground state constants are given in [1]. The ground state constants of NH_3-^{83}Kr (in italics) have been extrapolated from those of other Kr isotopes.

	^{82}Kr	^{83}Kr	^{84}Kr	^{86}Kr
		Σ_f (j=0,k=0)		
B''	2330.5543(1)	*2325.5*	2321.1770(1)	2312.2304(1)
D_J''	0.0457(1)	*0.0455*	0.0454(1)	0.0450(1)
		$\Pi_{e/f}$ (j=1,k=0)		
ν_0(cm^{-1})	951.55656(8)	951.55665(9)	951.55658(6)	951.55655(6)
B	2283.052(51)	2277.989(77)	2273.984(33)	2265.304(36)
B_{eff}	2316.43(12)	2311.34(19)	2307.048(76)	2298.11(8)
D_J	0.03766(31)	0.03632(70)	0.03765(14)	0.03731(19)
$D_{J,eff}$	0.05047(36)	0.05122(83)	0.04985(34)	0.04954(22)
H_J(10^6)	-2.08(5)	-4(1)	-1.69(18)	-1.69(27)
q	66.806(66)	66.76(11)	66.177(43)	65.657(47)
q_D	-0.01281(5)	-0.0149(13)	-0.0122(2)	-0.01213(3)
q_H(10^6)	5.0(1)	9(3)	4.2(3)	4.2(3)
R(Å)	3.9344(1)	3.9347(2)	3.93434(6)	3.93426(7)
ν_s (cm^{-1})	33.1(1)	32.8(3)	33.1(1)	33.0(1)
# lines	52	42	65	58
RMS	6.2	6.3	6.3	5.6

	NH_3-Ne		NH_3-Ar		NH_3-Kr		NH_3-Xe	
J	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*	Exp	*Ab initio*
1	284.87	*278.66*	97.16	*85.44*	61.48	*62.20*	83.47	*66.10*
2	284.91	*278.05*	91.44	*85.39*	65.99	*62.15*	85.65	*65.95*
3	284.94	*276.93*	91.71	*85.36*	66.37	*62.13*	82.99	*65.85*
4	284.95	*275.52*	91.66	*85.29*	65.99	*62.05*	83.79	*65.66*
5	284.96	*273.80*	92.39	*85.21*	66.33	*61.97*	82.82	*65.43*
6	283.12	*271.78*	92.05	*85.10*	65.63	*61.87*	82.01	*65.16*
7	283.09	*269.53*	92.26	*84.98*	66.00	*61.75*	81.34	*64.85*
8	282.01	*267.04*	92.33	*84.84*	66.44	*61.61*	80.77	*64.50*

Table S4: Energy difference between the *e* and *f* components of the $\Pi_{e/f}$ (*j*=1,*k*=0) state for *J* = 1-8 derived from the *ab initio* calculated VRT states (noted *Ab initio*) compared to the K-type doubling constant *q* extracted from the simplified expression of the rotational energy in Eqn (4) (noted Exp.)