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

Table S1: Calculated frequencies for the "short-bond" form of $CH_3CN–BCl_3$.[1]

*m*PW1[2]		B3PW91[3]		Symmetry[4]	Approximate Description
Wavenumber	Intensity	Wavenumber	Intensity		
32	0	31	0	A2	Torsion
70	2.4	70	2.4	E	Intermolecular bend
208	0.0090	207	0.0050	E	BCl3 asymmetric deformation
248	6.3	246	6.2	A1	B-N stretch
303	0.00010	301	0.00030	E	N-C-C bend
413	0.25	409	0.32	A1	BCl3 symmetric stretch
478	0.049	473	0.089	E	B-N-C bend
667	150	659	150	A1	BCl3 symmetric deformation
782	260	770	260	E	BC3l asymmetric stretch
1008	12	1001	10	A1	C-C stretch
1051	3.4	1046	3.2	E	C-C-N bend
1403	2.7	1396	2.6	A1	CH3 symmetric deformation
1457	14	1450	13.8	E	CH3 asymmetric deformation
2480[5]	73	2457[5]	64	A1	C-N stretch
3072	4.4	3054	3.9	A1	CH3 symmetric stretch
3157	3.8	3138	3.5	E	CH3 asymmetric stretch

1) Wavenumber values in units of cm^{-1}, intensities in km/mol. 2) With the aug-cc-pVTZ basis set. R(B-N)= 1.580 Å. 3)With the aug-cc-pVTZ basis set. R(B-N) = 1.581 Å. 4) Irreducible representation in the C_{3v} point group. 5) For a more thorough description of these motions see ref. 21. 6) No scale factor applied. See text for discussion.

Table S2: Calculated frequencies for the "long-bond" form of $CH_3CN–BCl_3$.[1]

*m*PW1[2]		B3PW91[3]		Symmetry[4]	Approximate Description
Wavenumber	Intensity	Wavenumber	Intensity		
9i	0	9i	0	A2	Torsion
17	5.4	16	5.4	E	Intermolecular bend
41	0.87	32	0.57	A1	B-N stretch
67	2.6	57	2.8	E	B-N-C bend
253	0.62	252	0.57	E	BCl3 asymmetric deformation
392	0.24	388	0.21	E	N-C-C bend
427	20	431	16	A1	BCl3 symmetric deformation
473	0.85	470	0.59	A1	BCl3 symmetric stretch
948	1.8	942	1.4	E	BC3l asymmetric stretch
957	330	948	330	A1	C-C stretch
1058	2.5	1053	2.3	E	C-C-N bend
1407	1.8	1400	1.8	A1	CH3 symmetric deformation
1471	11	1464	11	E	CH3 asymmetric deformation
2397[5]	18	2376[5]	16	A1	C-N stretch
3073	1.3	3056	1.7	A1	CH3 symmetric stretch
3153	0.060	3134	0.13	E	CH3 asymmetric stretch

1) Wavenumber values in units of cm^{-1}, intensities in km/mol. 2) With the aug-cc-pVTZ basis set. R(B-N)= 3.099 Å. 3)With the aug-cc-pVTZ basis set. R(B-N) = 3.237 Å. 4) Irreducible representation in the C_{3v} point group. 5) No scale factor applied. See text for discussion.