Normal Coordinate Analysis and Mean Amplitudes of Vibration in Acetonitrile-Boron Trifluoride

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A complete normal coordinate analysis for the complex acetonitrile-boron trifluoride has been carried out for the first time. Mean amplitudes of vibration, Bastiansen-Morino linear shrinkages, and the most important Coriolis coupling constants have also been determined.

Very recently a thorough vibrational study of acetonitrile-boron trifluoride [1], BF_3NCCH_3, has been given for the first time. The work [1] contains a normal coordinate analysis. It is not quite clear why we have not been able to reproduce exactly all of the calculated vibrational frequencies using the given force constants. One of the reasons may be an unsufficiently detailed specification of the applied valence coordinates. Nevertheless the reported force constants [1] were useful as a starting point in our normal coordinate analysis. We give here a detailed specification of the valence coordinates which were used to construct the symmetry coordinates. The final force field of the present analysis is given as the $\boldsymbol{F}$ matrix based on the symmetry coordinates.

As the main purpose of this work the developed force constants are used to compute mean amplitudes of vibration [2] and the linear shrinkage effects [2]. Calculated Coriolis coupling constants are also given.

Molecular Model

The calculations pertain to a free BF_3NCCH_3 molecule, for which a staggered C_{3v} structure is assumed; see Fig. 1. The structural parameters were taken from Ref. [1], viz.: $r = C-H = 1.157$ Å, $R = B-F = 1.347$ Å, $d = B-N = 1.630$ Å, $D = C\equiv N = 1.135$ Å, $L = C-C = 1.439$ Å; $\alpha = HCH$ and consequently $\beta = CCH$ were assumed to be the tetrahedral angles; $\delta = FBF = 113.13°$ gives a certain calculated angle for $\gamma = NBF$; the BNCC chain is linear.

The applied valence coordinates are specified in the following way with reference to the numbering of atoms as given in Fig. 1.

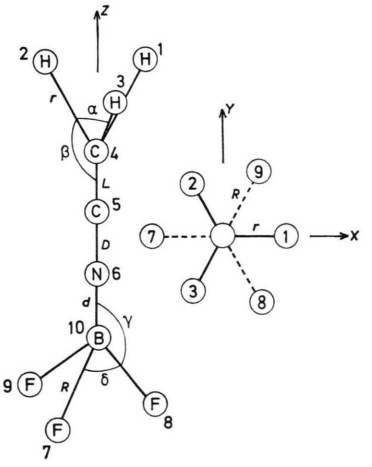

Fig. 1. The acetonitrile-boron trifluoride molecular model; symmetry C_{3v}.

Δr_i $(i = 1, 2, 3)$ for the C – H stretchings of the bonds $r_i(i-4)$; $\Delta L(4-5)$, $\Delta D(5-6)$ and Δd $(6-10)$ are the C – C, C≡N and B – N stretchings, respectively. ΔR_i represents the B – F stretchings of $R_1(7-10)$, $R_2(8-10)$ and $R_3(9-10)$.

$\Delta\alpha_i$ $(i = 1, 2, 3)$ for the HCH bendings of α_1 $(2-4-3)$, $\alpha_2(1-4-3)$ and $\alpha_3(1-4-2)$; $\Delta\beta_i$ for $\beta_i(i-4—5)$; $\Delta\delta_i$ for $\delta_1(8—10-9)$, $\delta_2(7-10-9)$ and $\delta_3(7-10-8)$; $\Delta\gamma_i$ for $\gamma_1(7-10-6)$, $\gamma_2(8-10-6)$ and $\gamma_3(9-10-6)$.

$\Delta\varepsilon_x$ and $\Delta\varepsilon_y$ are the linear NCC bendings in the X and Y directions; a positive $\Delta\varepsilon_x$ moves the cen-

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[1] B. SWANSON and D. F. SHRIVER, Inorg. Chem. **9**, 1406 [1970].

[2] S. J. CYVIN, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo, and Elsevier, Amsterdam, 1968.

tral C atom in the negative direction of the X axis. $\Delta\varrho_x$ and $\Delta\varrho_y$ are correspondingly the BNC linear bendings.

$\Delta\tau$ is a coordinate of internal rotation and taken as a combination of three torsions, viz.

$$-3^{-1/2}(\Delta\tau_{1,4,10,7}+\Delta\tau_{2,4,10,8}+\Delta\tau_{3,4,10,9}).$$

Symmetry Coordinates

Species A_1:

$$\begin{aligned}
S_1 &= 3^{-1/2}(\Delta r_1+\Delta r_2+\Delta r_3),\\
S_2 &= \Delta L,\\
S_3 &= \Delta D,\\
S_4 &= \Delta d,\\
S_5 &= 3^{-1/2}(\Delta R_1+\Delta R_2+\Delta R_3),\\
S_6^* &= 3^{-1/2}\,r(\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3),\\
S_6^{**} &= (r\,L/3)^{1/2}\,(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3),\\
S_7^{**} &= 3^{-1/2}\,R(\Delta\delta_1+\Delta\delta_2+\Delta\delta_3),\\
S_7^{**} &= (R\,d/3)^{1/2}\,(\Delta\gamma_1+\Delta\gamma_2+\Delta\gamma_3).
\end{aligned}$$

The final S_6 and S_7 coordinates are constructed using the relationship

$$S_j = m_j'\,S_j^* - m_j''\,S^{**} \qquad (j=6,7)$$

where m_j' and m_j'' are proper constant factors which make

$$m_j''\,S_j^* + m_j'\,S_j^{**} = 0$$

as the normalized zero coordinates. Numerically it was found

$$S_6 = 0.6676\,S_6^* - 0.7445\,S_6^{**}$$

and

$$S_7 = 0.6070\,S_7^* - 0.7947\,S_7^{**}.$$

Species A_2:

$$S_8 = (r\,R)^{1/2}\,\Delta\tau\,.$$

Species E (a):

$$\begin{aligned}
S_{9a} &= 6^{-1/2}(2\,\Delta r_1-\Delta r_2-\Delta r_3),\\
S_{10a} &= 6^{-1/2}(2\,\Delta R_1-\Delta R_2-\Delta R_3),\\
S_{11a} &= 6^{-1/2}\,r(2\,\Delta\alpha_1-\Delta\alpha_2-\Delta\alpha_3),\\
S_{12a} &= (r\,L/6)^{1/2}\,(2\,\Delta\beta_1-\Delta\beta_2-\Delta\beta_3),\\
S_{13a} &= 6^{-1/2}\,R(2\,\Delta\delta_1-\Delta\delta_2-\Delta\delta_3),\\
S_{14a} &= (R\,d/6)^{1/2}\,(2\,\Delta\gamma_1-\Delta\gamma_2-\Delta\gamma_3),\\
S_{15a} &= (L\,D)^{1/2}\,\varepsilon_x,\\
S_{16a} &= (D\,d)^{1/2}\,\varrho_x.
\end{aligned}$$

Species E (b):

$$\begin{aligned}
S_{9b} &= 2^{-1/2}(\Delta r_2-\Delta r_3,)\\
S_{10b} &= 2^{-1/2}(\Delta R_2-\Delta R_3),\\
S_{11b} &= 2^{-1/2}\,r(\Delta\alpha_2-\Delta\alpha_3),\\
S_{12b} &= (r\,L/2)^{1/2}\,(\Delta\beta_2-\Delta\beta_3),\\
S_{13b} &= 2^{-1/2}\,R(\Delta\delta_2-\Delta\delta_3),\\
S_{14b} &= (R\,d/2)^{1/2}\,(\Delta\gamma_2-\Delta\gamma_3),\\
S_{15b} &= (L\,D)^{1/2}\,\varepsilon_y,\\
S_{16b} &= (D\,d)^{1/2}\,\varrho_y.
\end{aligned}$$

The symmetry coordinates should differ only in a trivial manner from those of Ref. [1]: (a) the coordinate of internal rotation in species A_2 is included here, (b) the angle bendings are scaled by multiplying with constant factors with the dimension of length, and (c) the sequence differs; the present symmetry coordinates are arranged with respect to the types of valence coordinates, but irrespective of the wave numbers of the vibrational assignment.

Harmonic Force Field

After the detailed specification of the symmetry coordinates the harmonic force field may be given in a convenient way. Table 1 shows the A_1 and E

Table 1. Symmetry force constants (mdyne/Å) of acetonitrile-boron trifluoride.

							Species A_1	
1	5.042							
2	0.000	5.332						
3	0.000	0.001	18.877					
4	0.000	0.089	− 0.271	2.519				
5	0.000	0.000	− 0.001	0.739	6.532			
6	0.053	− 0.294	0.000	0.000	0.000	0.422		
7	0.000	0.000	0.000	− 0.491	0.307	0.000	0.610	
							Species E	
9	4.885							
10	− 0.023	2.767						
11	0.092	0.093	0.424					
12	0.200	0.048	0.010	0.403				
13	− 0.009	0.328	0.040	− 0.004	0.545			
14	0.003	0.289	− 0.021	0.003	− 0.099	0.631		
15	0.000	0.038	− 0.004	− 0.045	− 0.006	0.067	0.339	
16	0.000	0.006	− 0.002	− 0.001	− 0.001	− 0.001	0.015	0.097

Table 2. Observed [1] and calculated frequencies (cm^{-1}) for isotopic molecules of acetonitrile-boron trifluoride.

Frequency No.	^{11}B Obs.	^{11}B Calc.	^{11}BD Obs.	^{11}BD Calc.	$^{11}B^{15}N$ Obs.	$^{11}B^{15}N$ Calc.	^{10}B Obs.	^{10}B Calc.	^{10}BD Obs.	^{10}BD Calc.
1	2956	2956.0	2123.5	2123.2	2955.8	2956.0	2957.0	2956.0	2121.9	2123.2
2	2376.2	2376.2	2373	2379.3	2338.4	2343.7	2373.9	2376.3	2373.8	2379.4
3	1372.0	1372.0	1106.7	1121.3	1373.3	1371.8	1374.2	1372.0	1106.6	1121.4
4	978.7	978.7	892.2	883.5	968.7	967.9	979.0	980.2	899.8	899.5
5	869.5	869.5	863.9	864.1	879.0	869.5	883.8	889.8	886.6	870.0
6	651.4	651.4	647.5	647.3	654.6	651.5	660.5	663.2	655.9	658.9
7	359.2	359.2	348.7	347.7	356.1	357.5	358.6	359.3	347.8	347.9
9	3029.5	3029.5	2271	2253.6	3026	3029.5	3029	3029.5	2269	2253.6
10	1430	1430.0	1024.7	985.6	1420	1430.1	1430	1437.0	1025.7	988.6
11	1170	1170.0	1170	1215.9	1170	1169.6	1205.8	1212.5	1206	1262.5
12	1031.4	1031.4	848	857.3	1032	1031.1	1028.6	1031.5	850	857.3
13	520.9	520.9	518.8	501.6	516.0	512.1	522.0	520.9	518.7	501.7
14	422.8	422.8	407	397 9	417.7	422.6	422.2	423.2	406.5	398.2
15	314.3	314.3	298.6	312.0	312.8	313.8	313.9	314.3	298.1	312.0
16	98.5	98.5	97.3	93.5	—	97.6	100.1	98.5	98.0	93.6

blocks of the symmetry $\boldsymbol{F}$ matrix obtained as the final result of the present analysis. During several iterative steps the force constants were adjusted to fit exactly the observed frequencies [1] for $^{11}BF_3NCCH_3$.

The force constants developed here are practically the same as those of the previously reported force field [1] with two notable exceptions, for which we were not able to explain the discrepancies.

(1) $F_{33} = 0.585$ mdyne Å in the notation of Ref. [1] is not quite compatible with the corresponding value of 0.634 mdyne Å from the present analysis when based on unscaled angle bendings.

(2) The given B – F stretching constant [1], viz. 3.76 mdyne/Å is different from our value of 2.767 mdyne/Å.

Table 2 shows the calculated frequencies for several isotopic molecules of acetonitrile-boron trifluoride. The agreement with observed values [1] is generally good and comparable with the results of Ref. [1].

Coriolis Coupling Constants

The most important Coriolis coupling constants in a symmetrical top molecule are the first-order ones, which correspond to the diagonal elements of the $\zeta^z(E_a \times E_b)$ matrix. The force constants were used to calculate these quantities, and the results are given in Table 3.

Mean Amplitudes and Shrinkage Effects

The main purpose of this work was to compute mean amplitudes of vibration and the linear Bastiansen-Morino shrinkage effects for $^{11}BF_3NCCH_3$. It seems to be of special interest to establish a mean amplitude value of the unusual B – N bond between the two parts of the weak complex. Within the usual approximation of small harmonic vibrations the unknown torsional frequency (ν_8 of species A_2) has an influence only on one of the eighteen types of mean amplitudes. The calculated values for the remaining seventeen types of mean amplitudes are shown in Table 4. The calculated interatomic separations for each type of atom pairs are given (in Å units) in parentheses (R).

Table 3. First-order Coriolis coupling constants for isotopic molecules of acetonitrile-boron trifluoride. For the numbering of frequencies (species E), see Table 2.

No.	^{11}B	^{11}BD	$^{11}B^{15}N$	^{10}B	^{10}BD
9	0.203	0.311	0.203	0.203	0.311
10	– 0.314	– 0.373	– 0.314	– 0.246	– 0.410
11	0.844	0.852	0.844	0.778	0.891
12	0.450	0.549	0.449	0.450	0.549
13	0.724	0.575	0.720	0.723	0.573
14	0.291	0.236	0.278	0.290	0.236
15	– 0.660	– 0.601	– 0.654	– 0.660	– 0.601
16	0.597	0.576	0.607	0.597	0.576

The gauche-H ... F mean amplitude is highly dependent on the torsional frequency. Table 5 shows the calculated results for two values of ν_8, incidently chosen as 25 cm^{-1} and 150 cm^{-1}. It is to be expected that the applied aproximation of small harmonic vibrations fails at such low frequencies as 25 cm^{-1}.

The Bastiansen-Morino shrinkage effects for the linear BNCC chain are defined in the usual way [1],

Table 4. Mean amplitudes of vibration (Å units) for most of the distances in $^{11}BF_3NCCH_3$.

Distance	(R)	0 °K	298 °K
C—H	(1.157)	0.078	0.078
C—C	(1.439)	0.046	0.047
C≡N	(1.135)	0.034	0.034
B—N	(1.630)	0.058	0.061
B—F	(1.347)	0.050	0.053
N···C	(2.574)	0.049	0.050
B···C (short)	(2.765)	0.060	0.064
B···C (long)	(4.204)	0.066	0.071
C···H	(2.126)	0.104	0.105
N···H	(3.154)	0.119	0.123
B···H	(4.718)	0.134	0.155
N···F	(2.376)	0.060	0.067
C···F (short)	(3.384)	0.069	0.100
C···F (long)	(4.745)	0.084	0.139
H···H	(1.889)	0.128	0.128
F···F	(2.248)	0.062	0.073
trans-H···F	(5.496)	0.122	0.136

Table 5. Mean amplitudes of vibration (Å units) for the gauche-H...F distance in $^{11}BF_3NCCH_3$; interatomic separation: 5.095 Å.

ν_8 (cm^{-1})	0 °K	298 °K
25	0.189	0.490
150	0.163	0.242

and may all be calculated independent of the torsional frequency. The results are given in Table 6.

Table 6. Bastiansen-Morino shrinkage effects (Å units) in $^{11}BF_3NCCH_3$.

Distance	0 °K	298 °K
N···C	0.0057	0.0072
B···C (short)	0.0073	0.0175
B···C (long)	0.0133	0.0328

Concluding Remarks

The present calculations of mean amplitudes and shrinkage effects would be of great interest in a possible electron diffraction investigation of the molecule in question. This method has also proved to be useful in the studies of the phenomenon of internal rotation. In connection with such studies the present calculations might be pursued to determine the framework mean amplitudes as functions of the angle of internal rotation. The case would be especially convenient for such computations because the torsional frequency, which pertains to the internal rotation, is completely separated from all the other normal modes by virtue of symmetry.

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Kathodolumineszenzabklingen von KJ und KJ(In) oberhalb 78 °K

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Decay of Cathodoluminescence of KJ and KJ(In) above 78 °K

The lifetimes of cathodoluminiscence of KJ and KJ(In) were investigated above 78 °K. The dependence of irradiation was compared with the production of traps; the measurements showed some correlation between the lifetime and the ratio of concentrations of M- and F-centers. This correlation is confirmed by a reactionkinetical model.

Einleitung

Das Eigenlumineszenzspektrum von Kaliumjodid-Kristallen enthält bei Temperaturen um 80 °K zwei Banden der Wellenlängen 371 nm und 302 nm; diese Banden treten auf bei optischer Erregung oberhalb der Bandkante, bei Erregung mit ionisierender Strahlung und bei Ausleuchtung nach Erregung mit ionisierender Strahlung bei 80 °K. Der Prozeß der 371 nm-Lumineszenz läßt sich folgendermaßen beschreiben[1]: durch den Einfang freier Elektronen in lokalisierte Löcher (V_k-Zentren) bilden

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[1] H. BLUME, P. BRAUER u. G. STÜHMER, Z. Naturforsch. **21 a**, 849 [1966].