

FTIR studies of the CH₃CN–BF₃ complex in solid Ar, N₂, and Xe: Matrix effects on vibrational spectra

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Received 30 January 2005; revised 22 April 2005; accepted 24 April 2005

Available online 14 June 2005

Abstract

FTIR spectra of the four isotopically substituted 1:1 complexes of acetonitrile and boron trifluoride were recorded in Ar, N₂ and Xe matrices. In Ar, previously unreported three vibrational modes of the complex were clearly observed. Several significant vibrational bands were also observed in N₂ and Xe. The observed frequency shifts on complexation, $\Delta\nu$, were qualitatively in good agreement with the computational results, which were calculated at the B3LYP/6-311++G(d,p) level using the optimized geometry of the C_{3v} eclipsed conformation. The observed magnitudes of $\Delta\nu$ for most of the complex bands were larger than the calculated values. The BF₃ symmetric deformation mode is an exception. The observed frequency shifts for this mode were smaller than the calculated values, especially in N₂. This suggests that even an inert matrix can significantly affect the vibrational spectrum of the complex.

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Keywords: Matrix isolation; Infrared spectroscopy; Matrix effects; Acetonitrile; Boron trifluoride

1. Introduction

Structures and bondings of the electron donor-acceptor (EDA) complexes containing boron trifluoride have been the subject of many experimental [1–11] and theoretical [12–15] studies. After the first preparation of the 1:1 adduct of boron trifluoride with acetonitrile [16], it has attracted attention for its significant difference of the B–N bond lengths between the crystalline and the gas phases [17–23]. X-ray crystallography showed that the B–N bond length and the FBN bond angle of CH₃CN–BF₃ in the crystalline solid were 1.630 Å and 105.6°, respectively [19]. On the other hand, Dvorak et al. investigated the microwave spectra of the complex in the gas phase [21]. They reported that the B–N bond length and the FBN bond angle in the gas phase were 2.011 Å and 95.6°, respectively, based on the analysis in which other structural parameters were constrained to the values of the component monomers. Theoretical studies on the structure of the complex including medium effects have also been published [24–29]. The MP2 calculation with

a reasonable basis set [28] showed the B–N bond length of 1.8008 Å and the FBN bond angle of 101.20°, both of which are intermediate between the crystalline and the gas phase values.

Recently, Giesen et al. precisely studied the structure of the CH₃CN–BF₃ complex, especially the difference between the gas phase and the theoretical results, and the characteristics of the BN bond by the MP2 and B3LYP levels of calculations with larger basis sets [29]. According to their results, two local minima along with the B–N distance were obtained at the B3LYP level using sufficiently large basis sets. The longer B–N length of 2.315 Å was the global minimum for the largest aug-cc-pVQZ basis. However, the energy difference between the two minima is lower than 0.2 kcal/mol and the potential curve along with the B–N coordinate is extremely flat from 1.8 to 2.5 Å. They suggested that the difference between the B–N distance averaged over this flat potential and the equilibrium bond length is responsible for the discrepancy between the gas phase and the theoretical structures.

The vibrational spectra of the CH₃CN–BF₃ complex were also observed in the solid phase [18,20] and the Ar matrix [22,23]. The blue shift of the CN stretching mode on complexation and the characteristics of the BN bond have been the matters of interest. Comparisons of the calculated

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and the experimental vibrational frequencies were also reported [28,29]. Roughly speaking, the vibrational frequencies of the complex in an Ar matrix are similar to the calculated values rather than the frequencies in the crystalline phase. This seems to indicate the structural similarity between the calculated and the matrix isolated complexes. Giesen et al. [29], however, suggested that the B–N bond length of the complex in an Ar matrix is somewhat shorter than that of the short minimum geometry (1.919 Å) optimized at the B3LYP/aug-cc-pVQZ level. They investigated the effect of Ar matrix environment on the equilibrium geometry of the complex using the SCRF CPCM model, and showed the significant shortening of the B–N bond length, which indicates that even a very low dielectric medium can dramatically change the shape of the B–N potential surface.

Vibrational spectroscopic studies of the CH₃CN–BF₃ complex in matrices other than Ar are expected to give more information about the matrix effects on the structure and vibrational frequencies of the complex. In this paper, we present the FTIR spectra of the CH₃CN–BF₃ complex including its isotopically substituted species in solid N₂ and Xe, together with some previously unreported vibrational modes in Ar. Matrix effects on the vibrational spectra, especially the frequency shift on complexation are also discussed.

2. Experimental and computational methods

BF₃ (99.99%) was purchased from Takachiho Chemical Industrial Co., Ltd. ¹⁰BF₃ was prepared from ¹⁰B₂O₃ (Aldrich, 99%) and Na¹⁰BF₄ [30], which was prepared by mixing of HF (Morita Chemical Industries Co., Ltd.), H₃¹⁰BO₃ (Aldrich, 99%) and Na₂CO₃ (Kanto Kagaku, 99.5%). CH₃CN (99.5%) and CD₃CN (99.8%) were purchased from Wako Pure Chemical Industries, Ltd. and Aldrich, respectively. All samples were purified by the trap-to-trap method in an all-glass vacuum line. Matrix gases, Ar (Nippon Sanso, 99.9995%), N₂ (Nippon Sanso, 99.9995%) and Xe (Takachiho, 99.99%), were used without further purification. The mixtures of CH₃CN and BF₃ with excess matrix gases were prepared using standard manometric techniques. CH₃CN/M and BF₃/M (M=Ar, N₂) were co-deposited on a CsI plate maintained at 20 or 12 K. Subsequent annealing procedures were carried out at 33 K. For CH₃CN/Xe and BF₃/Xe, co-deposition and annealing temperatures were 30 and 60 K, respectively. The cryostat used was CTI Cryogenics LT-21, coupled with Tristan Technologies, Inc. LTC-20 temperature controller. Reagent/matrix ratios (R/M) were in the range of 1/200–1/400. All spectra were recorded on a Nicolet Magna 750 FTIR spectrometer, in the wavenumber range from 4000 to 400 cm⁻¹ at 1 cm⁻¹ resolution.

The MP2 and B3LYP calculations were carried out with several basis sets of valence triple-zeta level using

Gaussian03 program [31]. Geometry optimizations were performed using the ‘opt=verytight’ option. Harmonic vibrational frequencies were calculated numerically for MP2 and analytically for B3LYP.

3. Results and discussion

3.1. Optimized geometry and harmonic frequencies of the CH₃CN–BF₃ complex

Several computational studies on the structure and the vibrational frequencies of the CH₃CN–BF₃ complex have been published previously [24–29]. However, we had to know the calculated harmonic frequencies of some isotopically substituted species, which can be used for the vibrational assignment of all the observed frequencies. Therefore, we also calculated the optimized geometry and the harmonic frequencies of the complex at the MP2 and B3LYP levels with some standard basis sets. According to the previous studies [28,29], the eclipsed conformation with C_{3v} symmetry was assumed during the geometry optimization. The important geometrical parameters of the 1:1 CH₃CN–BF₃ complex are presented in Fig. 1. The optimized values of these parameters and the harmonic frequencies for the CH₃CN–¹¹BF₃ species are compared with previously reported results in Tables 1 and 2. Note that the mode numbering scheme in Table 2 is that from Cho et al. [28].

Table 1 shows that the B–N bond length and the FBN bond angle have somewhat large dependence on the level of calculation. A significant shortening of the B–N bond length on introducing the diffuse functions [29] was also found for our basis sets. For B3LYP, most of the geometrical parameters calculated with the 6-311++G(d,p) and 6-311G(d,p) basis sets are similar to those calculated with the larger aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively. However, the B–N bond length at the B3LYP/6-311++G(d,p) level is somewhat shorter than that at the B3LYP/aug-cc-pVTZ, and closer to the value at the MP2/6-31++G(2d,p) level. The B–N, CN and CC bond lengths at the B3LYP level are slightly shorter than those at the MP2 level with the same basis set. The CN and CC bond lengths of the CH₃CN monomer in the gas phase are 1.1572 and 1.4596 Å, respectively [32]. Since the shortenings of these bonds are expected on complexation, the B3LYP

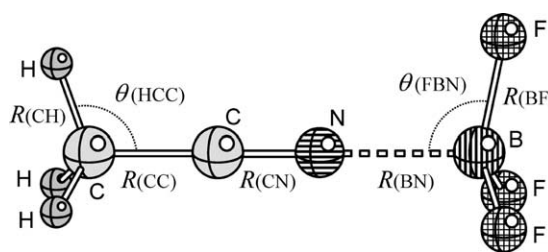


Fig. 1. Optimized geometry of the 1:1 CH₃CN–BF₃ complex. Determined values of geometrical parameters are listed in Table 1.

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