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Ab initio molecular orbital studies of the vibrational spectra of the van der Waals complexes of boron trifluoride with the noble gases

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Abstract

The molecular structures, interaction energies, charge transfer properties and vibrational spectra of the van der Waals complexes formed between boron trifluoride and the noble gases neon, argon, krypton and xenon have been computed using second and fourth order Møller–Plesset perturbation theory and the Los Alamos National Laboratory LANL2DZ basis set. The complexes are all symmetric tops, with the noble gas atom acting as a σ electron donor along the C_3 axis of the BF_3 molecule. The interaction energies are all vanishingly small, and the amount of charge transferred in each case is of the order of 0.01*e*. The directions of the wavenumber shifts of the symmetric bending (ν_2) and antisymmetric stretching (ν_3) modes of the BF_3 fragment confirm those determined experimentally, and the shifts are shown to correlate well with the polarizability of the noble gas atom and the inverse sixth power of the intermonomer separation. The ν_2 mode is substantially more sensitive to complexation than the ν_3 vibration.

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1. Introduction

A number of recent publications from this laboratory have reported our ab initio calculations of the vibrational properties of the binary electron donor–acceptor complexes of boron trifluoride with a variety of oxygen, nitrogen and sulphur bases. The computed binding energies of these complexes have been found to lie in the range from 3.486 kJ mol^{-1} for the eclipsed O-bound isomer of $BF_3{\cdot}N_2O$ [1] to 60.68 kJ mol^{-1} for staggered $BF_3{\cdot}NH_3$ [2], using second order Møller–Plesset perturbation theory [3] and the 6–31G(d) [1] or 6–31G(d,p) [2] basis sets [4]. In each case the interaction energies were corrected for basis set superposition error (BSSE) [5]. We were interested to determine whether ab initio calculations, at a similar level of theory, were capable of reproducing such experimental data as exist for those very weakly bound complexes at the extreme low interaction energy end of the spectrum. As examples of these weak complexes we selected for study the adducts of boron trifluoride with the noble gases neon, argon, krypton and xenon.

The $BF_3{\cdot}Ar$ complex was first detected in the gas phase by Novick et al. by means of molecular beam electric deflection measurements in the radiofrequency region, using a supersonic nozzle [6]. They concluded that the complex was polar, most likely a symmetric top, and possessed a dipole moment of about 0.2 D. These measurements were later extended to molecular beam electric resonance experiments in the microwave region by Janda et al., also using supersonic expansion, who confirmed that the complex was a symmetric rotor [7]. They were able to refine the value of the measured dipole moment to 0.176 D, and determined the B rotational constants of the ^{10}B- and ^{11}B-containing isotopic species, from which they calculated the B···Ar van der Waals bond length to be 332.5 pm. The nature of the complex was characterized as resulting from a quadrupole-induced dipole interaction, with electron transfer in the direction Ar → B. The nature of the Ar atom as a σ donor was confirmed by Burdett, on the basis of a simple molecular orbital treatment, who proposed

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that the angular geometry was determined largely by covalent, rather than van der Waals forces [8]. Fowler and Stone, using a distributed multipole and distributed polarizability analysis, computed the induced dipole moment of $BF_3 \cdot Ar$ to be 0.186 D [9], in quite good agreement with the experimental value of Janda et al., and concluded that the origin of the dipole moment was inductive, although they pointed out that the binding forces themselves were predominantly dispersive. A similar conclusion was reached by Kisiel, who employed a model consisting of dispersive attractive and hard sphere repulsive terms, and estimated a well depth of 163.6 cm^{-1} (1.957 kJ mol^{-1}) [10].

The first examples of BF_3 complexes containing noble gases other than Ar were those with Ne, Ar and Kr, studied by high resolution vibration–rotation spectroscopy of supersonic jets using frequency-tunable diode laser detection in the BF_3 monomer degenerate stretching region, reported by Takami et al. [11]. The monomer absorption was red-shifted, the wavenumber shifts correlating linearly with the noble gas atom polarizability. This work was later amplified by Matsumoto et al., who confirmed the symmetric top structure of the three complexes and deduced values for the ground state B rotational constants and the van der Waals bond lengths [12]. They also found that the BF_3 monomer wavenumber shifts were proportional to the ratio of the polarizability to the sixth power of the van der Waals bond length. The same group extended their measurements to the BF_3 monomer symmetric bending region, in which the shifts were found to be about three times larger than in the antisymmetric stretching region, and confirmed the linear dependence of the shifts [13,14].

In this work, we report the structures, interaction energies and vibrational wavenumber shifts on complexation of the three complexes studied experimentally, and extend our calculations to the fourth member of the series, $BF_3 \cdot Xe$, which has not yet been subjected to experimental study, in an attempt to reproduce the relationships reported earlier [11–14].

2. Computational procedure

The calculations were carried out using the Gaussian-98 computer program [15], at the second (MP2) [3] and fourth (MP4(SDQ)) orders of Møller–Plesset perturbation theory with single, double and quadruple substitutions [16,17]. For consistency, the LANL2DZ basis set for B, F and Ne [18], with the Los Alamos effective core potential (ECP) for Ar, Kr and Xe, was used [19–21]. Geometry optimizations were performed, subject to C_{3v} symmetry, as suggested by the experimental structure of $BF_3 \cdot Ar$ [6,7,11–14], using the tightest convergence criterion available. Fig. 1 shows the optimized structure of the $BF_3 \cdot Ar$ complex, determined at the MP4(SDQ) level. Interaction energies were calculated, relative to the relaxed monomer species, and were corrected for BSSE [5] by the full counterpoise correction procedure of Boys and Bernardi [22]. Corrections for vibrational zero-point energy difference were also applied. Rotational constants and dipole moments were computed at the equilibrium geometries, for comparison with experimental values. Vibrational analyses confirmed that each converged structure was a genuine minimum, and the wavenumbers (and their shifts relative to the BF_3 monomer wavenumbers) and infrared intensities (and their ratios to the monomer intensities) of the complexes were calculated.

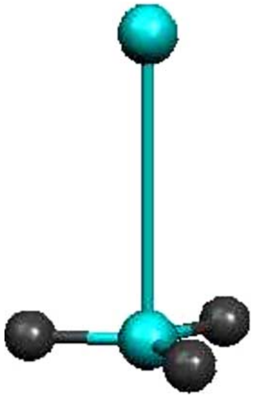

Fig. 1. Optimized structure of the $BF_3 \cdot Ar$ complex (MP4(SDQ) calculations).

3. Results and discussion

3.1. Interaction energies

The calculations were carried out initially at the MP2 level. The differences between the optimized energies of the complexes and the computed energies of the relaxed BF_3 and Rg species (Rg = Ne, Ar, Kr, Xe) are presented in Table 1. This

Table 1
Computed interaction energies (MP2/LANL2DZ and MP4(SDQ)/LANL2DZ) of the BF_3–noble gas van der Waals complexes

Complex	Interaction energy (kJ mol^{-1})				Well depth[a] (kJ mol^{-1})
	MP2		MP4(SDQ)		
	Uncorrected	Corrected[b]	Uncorrected	Corrected[b]	
$BF_3 \cdot Ne$	−3.004	0.426	−10.781	0.455	
$BF_3 \cdot Ar$	−2.405	0.270	−2.714	0.352	−1.957
$BF_3 \cdot Kr$	−2.520	0.523	−2.936	0.651	
$BF_3 \cdot Xe$	−1.475	0.231	−1.769	0.301	

[a] See Ref. [10].

[b] Corrected for BSSE.

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