The Anharmonic Force Field of BeH_2 Revisited

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Abstract

The anharmonic force field of BeH_2 has been calculated near the basis set and n-particle space limits. The computed antisymmetric stretch frequencies of BeH_2 and BeD_2 are in excellent agreement with recent high-resolution gas-phase measurements [P. F. Bernath et al., Science **297**, 1323 (2002)]. The agreement between theory and experiment for the other spectroscopic constants is also excellent, except for ω_3 and X_{33} for BeH_2 and G_{22} for BeD_2. It is concluded that further experimental work is needed in order to resolve these discrepancies.

Introduction

Recently, Bernath and coworkers reported the first high-resolution rovibrational band assignment for polyatomic molecules containing beryllium, BeH_2 and BeD_2 [1,2]. Beryllium vapor is known to be very toxic, which probably explains why there have been very few gas-phase experimental studies on beryllium-containing polyatomic molecules to date. Nonetheless, BeH_2 has been the target of several theoretical studies [3-5] over the years, partly because it has only four valence electrons and thus is an ideal test molecule for new electron correlation methods. BeH_2 has been the subject of very accurate theoretical studies, such as Ref. [3], where a quartic force field, equilibrium geometry, and fundamental vibrational frequencies were computed using the CCSD(T) method [6] (singles and doubles coupled-cluster theory with a perturbational estimate of connected triple excitations). High-level *ab initio* calculations have also shown that BeH_2 is thermodynamically stable [4] relative to dissociation to Be + H_2 (37.6 kcal/mol), but direct insertion of a beryllium atom into the H_2 bond has a barrier of 48.6 kcal/mol [5].

The ν_2 and ν_3 bands of BeH_2 and BeD_2 were first observed [7] in an argon matrix infrared (IR) study of reaction products of H_2 with beryllium atoms generated by pulsed laser evaporation.

Bernath and coworkers' assignment for the antisymmetric Be-H stretch, ν_3, was aided by the aforementioned CCSD(T) study of the fundamental vibrational frequencies [3]. In this case, the theoretical calculations predicted a fundamental vibrational frequency of 2167.2 cm^{-1}, which compares reasonably well with the experimental assignment of 2178.8 cm^{-1}. (The latter, incidentally, implies a sizeable Ar matrix red shift

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of 19.7 cm^{-1} in Ref.[7].) However, the calculations in Ref. [3] included only the valence electrons in the CCSD(T) correlation procedure and only considered up through *f*-type functions in the one-particle basis set. There is ample evidence now to indicate that the majority of the remaining error in valence CCSD(T) calculations is due to the neglect of core correlation, and this is even more likely to be the case for beryllium compounds due to the well known near degeneracy between the 1*s* and 2*s* shells (for example, see Refs. [8-12]). The primary purpose of this study is to present state-of-the art calculations of the quartic force field, equilibrium structure, and fundamental vibrational frequencies for BeH_2 in order to assess the level of accuracy that is obtainable for polyatomic beryllium compounds from purely *ab initio* calculations. This study therefore includes the effects of core correlation and the use of one-particle basis sets that go beyond *f*-type functions, as well as valence correlation that goes beyond CCSD(T) and scalar relativistic contributions, of which the latter two are expected to be smaller effects.

The theoretical approach is detailed in the next section followed by results and discussion. The final section contains our conclusions.

Theoretical Approach

Most electronic structure calculations have been carried out using the MOLPRO 2002.3 electronic structure system [13]. The CCSD(T) [6] electron correlation method was used for most calculations. For *n*-particle calibration purposes, CCSDT (coupled cluster with all single, double, and triple excitations [14]) and FCI (full configuration interaction) calculations were also carried out, the former using the Austin-Mainz version of ACES II [15], the latter by means of the Handy-Knowles determinantal FCI code [16] in MOLPRO.

Standard Dunning cc-pVnZ (correlation consistent polarized valence n-tuple zeta [17]) basis sets were used throughout on hydrogen. Some calculations in which only valence electrons were correlated employed preliminary cc-pV*nZ* basis sets for beryllium [18]; for calculations in which all electrons were correlated, the CV*nZ* (core-valence *n*-tuple zeta) basis sets for beryllium were taken from a recent paper on core-valence correlation in the alkali and alkaline earth metals [19].

Scalar relativistic effects were considered by means of the Douglas-Kroll approximation [20,21] as implemented in MOLPRO 2002.3.

Spectroscopic constants for the molecule were obtained using standard second-order rovibrational perturbation theory [22] as implemented in the SPECTRO [23,24] program.

Results and Discussion

A. Spectroscopic Constants for BeH_2

Computed and observed anharmonic spectroscopic constants are presented in Table 1. Computed geometries and harmonic frequencies at some additional levels of theory can be found in Table 2.

Using the cc-pVTZ basis set (i.e. $4s3p2d1f$ on Be and $3s2p1d$ on H), we were able to carry out valence FCI calculations, which are an exact solution of the nonrelativistic Schrödinger equation in the given one-particle basis set. As expected for a molecule like

BeH_2 which is dominated by a single reference configuration, the CCSD(T) data with the same basis set are in very close agreement with FCI. The chief differences are that CCSD(T) apparently overestimates the three fundamental frequencies by 1.5, 0.4, and 1.1 cm^{-1}, respectively, and underestimates the bond distance by 0.00015 Å. The largest anharmonicity constant, X_{13}, is underestimated (in absolute value) by 0.13 cm^{-1}. Higher-order effects of connected triple excitations account for essentially all of the difference: the CCSDT and FCI data are nearly indistinguishable.

As the basis set is enlarged to *5s4p3d2f* on Be and *4s3p2d* on H (i.e., cc-pVQZ without *g* functions on Be nor *f* functions on H), the differences between CCSD(T) and FCI actually *decrease* for the frequencies, although the tiny geometric difference remains constant. This confirms that CCSD(T) is a suitable level of theory for treating the system.

As expected, scalar relativistic effects are nearly nonexistent in this very light system: the only changes seen upon introducing Douglas-Kroll corrections are a further shortening of the bond distance by 0.0001 Å and a decrease in the bending frequency by 0.1 cm^{-1}.

As could be expected for this system based on previous experience with BeH [9], inner-shell correlation effects are quite prominent. Comparing CCSD(T)/CVQZ force fields with and without Be(1*s*) correlation, we find that the latter shortens the bond by about 0.004 Å and increases the fundamental frequencies by 8, 3, and 9 cm^{-1}, respectively. In fact, the CCSD(T)/CVQZ spectroscopic constants are in excellent agreement with the available experimental data: ν_3 is reproduced to within 0.5 cm^{-1} and r_e to four decimal places, while X_{13} and X_{23} agree to 0.25 and 0.06 cm^{-1}, respectively. The fairly small discrepancy in G_{22} might be eliminated if more experimental data involving ν_2 were available. Agreement is equally satisfying for the centrifugal distortion and l-doubling constants. Disagreements (with opposite signs) of 0.001 cm^{-1} are seen in α_1 and α_2. These could reflect either contributions of higher-order rovibrational coupling in the experimental data, nonadiabatic effects (which are somewhat significant for the BeH bond distance [9]), or a combination of both.

In light of the generally excellent agreement between theory and experiment — particularly for ν_3 — the fact that our computed ω_3 exceeds the experimentally derived value by nearly 5 cm^{-1} is somewhat puzzling. The phenomenon appears to be linked with a discrepancy of –2 cm^{-1} (theory predicting the larger absolute value) for X_{33}. It is extremely unlikely that further improvement of the theoretical treatment will cause substantial changes in the computed X_{33}. Furthermore, no resonances exist and the molecule is rigid enough for a second-order rotation-vibration perturbation theory treatment to be adequate. We note that the experimental value — obtained from $[G(00^02)-2G(00^01)]/2$ — is an effective one that includes higher-order anharmonicity contributions, $X_{33}^{eff}=X_{33}+Y_{133}/2+Y_{233}+9Y_{333}/2+O(Z_{ijkl})$. Y_{333} can be estimated from $[G(00^03)-3G(00^02)+3G(00^01)]/6=Y_{333}+O(Z_{ijkl})$. If we assume the third anharmonicities to be negligible, then Y_{333} is found to be –0.107 cm-1, nearly identical to the best computed $\omega_e y_e$ for BeH [9]. This suggests either unusually large Y_{133} and Y_{233} constants, or a problem with X_{33} itself. Further experimental work would certainly be useful for clarifying this issue.

At the CCSD(T)/CVTZ level, ν_2 is calculated to have an infrared intensity of 472.8×2 km/mol, compared to 274.2 km/mol for the antisymmetric stretch which *was* observed. This certainly suggests the ν_2 band ought to be amenable to experimental study in the gas phase.

As noted previously [9,10], the anharmonicity constants are rather more sensitive to the basis set than generally assumed. Their sensitivity to inner-shell correlation is rather minor, reflecting mostly the changes in the underlying harmonic frequencies. Table 1 suggests, however, that the CCSD(T)/CVQZ values are largely converged with the computational level of theory, and that observed values for the missing constants are unlikely to deviate substantially from our computational predictions.

Further basis set expansion to CV5Z leads to a shortening of the bond by 0.0003 Å (half of which cancels with inclusion of higher-order correlation effects), and minor changes in the computed frequencies that largely cancel with inclusion of higher-order triple excitation effects.

B. Spectroscopic Constants for BeD_2

Agreement between CCSD(T)/CVQZ and experiment for the ν_3 fundamental of BeD_2 bolsters our conclusions about the quality of the BeH_2 force field. Indeed, the difference here is only 0.2 cm^{-1} versus 2.1 cm^{-1} for BeH_2. For BeD_2, the main disagreement with experiment is for G_{22}, which is computed nearly an order of magnitude larger than the experimental value. Again, this suggests that further experimental work on the bend is in order, especially considering the excellent agreement for ν_3, a direct observable.

Conclusions

A highly accurate anharmonic force field for BeH_2 has been computed, and is capable of reproducing the observed data with near-spectroscopic accuracy. The principal shortcoming of the earlier calculation [3] was neglect of inner-shell correlation: the effect of higher-order connected triple excitations is an order of magnitude less important, and the effects of connected quadruple excitations and of relativity can be neglected outright. Some issues with the experimentally derived harmonic antisymmetric stretching frequency and the associated anharmonicity for BeH_2 suggest further experimental work may be in order, as does the l-type resonance constant G_{22} for BeD_2. The bending frequency is predicted to be very intense and should be amenable to experimental observation.

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Supporting information

The computed quartic force field of BeH_2 is available for download, in a variety of coordinate systems, at http://theochem.weizmann.ac.il/web/papers/BeH2.html

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Table 1. Spectroscopic constants (Å and cm^{-1}) for BeH_2 and BeD_2.

	BeH_2							BeD_2	
	Expt[a]	CCSD(T)	CCSD(T)		CCSD(T)	CCSDT	FCI	CCSD(T)	Expt[a]
		CV5Z	CVQZ		VTZ	VTZ	VTZ	CVQZ	
		all[b]	all[b]	val[c]	val[c]	val[c]	val[c]	all[b]	
$\omega_1(\sigma_g)$		2050.8	2050.7	2042.2	2029.2	2028.1	2027.9	1450.7	
$\omega_2(\pi_u)$	716.5	716.5	717.1	714.0	709.0	708.6	708.6	551.6	
$\omega_3(\sigma_u)$	2255.155(1)	2260.2	2260.0	2250.4	2237.9	2237.0	2236.8	1738.5	
$\nu_1(\sigma_g)$		1994.6	1993.3	1985.1	1976.3	1975.0	1974.8	1426.4	
$\nu_2(\pi_u)$	[d]	713.6	712.7	709.6	708.0	707.6	707.6	548.9	[e]
$\nu_3(\sigma_u)$	2178.8659(2)[d]	2180.8	2179.4	2170.2	2160.6	2159.6	2159.5	1689.9	1689.6788(3)[e]
X_{11}		-13.870	-13.885	-12.980	-12.921	-12.959	-12.978	-6.948	
X_{12}		0.285	-0.173	-0.178	0.756	0.718	0.719	+5.076	
X_{13}	-58.7127(3)	-57.637	-58.959	-58.631	-55.694	-55.811	-55.821	-30.963	
X_{22}		0.258	-0.129	-0.093	0.801	0.809	0.806	-1.055	
X_{23}	-12.9834(3)	-12.809	-13.048	-12.980	-12.193	-12.212	-12.213	-9.224	-9.0905(5)
X_{33}	-16.9745(3)	-18.873	-19.016	-18.912	-18.595	-18.622	-18.633	-11.924	-11.3111(4)
G_{22}	2.050	2.476	2.602	2.570	2.321	2.316	2.317	+2.522	0.150(2)
r_e	1.326407(3)	1.326157	1.326450	1.330713	1.333911	1.334037	1.334061	1.326450	
r_0	1.333758(1)	1.333316	1.333627	1.337915	1.340839	1.340970	1.340972	1.331530	1.331361(4)
r_z		1.336313	1.336626	1.340915	1.343835	1.343981	1.344008	1.333752	
r_g		1.347082	1.347385	1.351687	1.354656	1.354807	1.354834	1.342028	
B_e	4.75366(2)	4.75545	4.75335	4.72294	4.69943	4.69927	4.70032	2.37862	
B_0		4.70452	4.70232	4.67223	4.65100	4.65081	4.65200	2.36051	
α_1	0.05698(2)	0.05582	0.05584	0.05545	0.05341	0.05343	0.05328	0.01977	–
α_2	-0.01084(1)	-0.01173	-0.01163	-0.01151	-0.01222	-0.01221	-0.01223	-0.00719	-0.00686(2)

α_3	0.06921(1)	0.06950	0.06947	0.06897	0.06790	0.06792	0.06781	0.03084	0.03070(2)
10^4D_e	1.0212(5)	1.0230	1.0218	1.0106	1.0095	1.0096	1.0090	0.25586	
10^9H_e	2.39(3)	2.55	2.54	2.50	2.57	2.57	2.57	0.3	
q_{010}	-0.09141(1)	-0.09133	-0.09123	-0.09046	-0.09014	-0.09014	-0.09014	-0.02970	-0.03018(4)

[a] From Table V in Ref. [2].

[b] All electrons were included in the correlation procedure.

[c] Only the valence electrons were included in the correlation procedure.

[d] In Ar matrix: ν_2=697.9, ν_3=2159.1 cm^{-1} [7].

[e] In Ar matrix: ν_2=531.9, ν_3=1674.0 cm^{-1} [7].

Table 2. Equilibrium bond distance (Å) and harmonic frequencies (cm^{-1}) for BeH_2.

	FCI	CCSD(T)	CCSDT	DK-CCSD(T)	CCSD(T)
	VQZ(spdf)	VQZ(spdf)	VQZ(spdf)	CV5Z	CV5Z
	val[a]	val[a]	val[a]	all[b]	all[b]
r_e	1.331124	1.330979	1.331101	1.326055	1.326157
$\omega_1(\sigma_g)$	2040.6	2041.2	2040.2	2050.8	2050.8
$\omega_2(\pi_u)$	712.8	713.2	712.8	716.7	716.6
$\omega_3(\sigma_u)$	2248.6	2249.5	2248.8	2260.2	2260.2

[a] All electrons were included in the correlation procedure.

[b] Only the valence electrons were included in the correlation procedure.