

Geometry, Vibrational Frequencies, and Ionization Energies of BeX<sub>2</sub> (X = F, Cl, Br, and I)Edmond P. F. Lee<sup>†,‡,§</sup> and Timothy G. Wright<sup>\*,||</sup>

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The equilibrium geometries and harmonic vibrational frequencies of BeF<sub>2</sub>, BeCl<sub>2</sub>, BeBr<sub>2</sub>, and BeI<sub>2</sub> are calculated. For the lighter two molecules, only all-electron methods were used, whereas for the heavier two, all-electron and effective core potential (ECP) methods were used. MP2, QCISD, and B3LYP calculations were employed, and it was found that the combination of ECPs (with a suitable valence basis set) with the B3LYP density functional method is a relatively inexpensive means of obtaining reliable information on these species. All four molecules were found to be linear, in agreement with simple molecular orbital ideas. The lowest electronic states are calculated using the configuration interaction with single excitations approach. Finally the adiabatic and vertical ionization energies of the BeX<sub>2</sub> species are calculated. For BeF<sub>2</sub> and BeCl<sub>2</sub>, the first vertical ionization energy (VIE) was calculated at the CASSCF+MRCI level, and the lowest four VIEs were calculated at the CCSD(T) level using large basis sets: for BeCl<sub>2</sub> comparison with the photoelectron spectrum is presented. For BeBr<sub>2</sub> and BeI<sub>2</sub>, the lowest VIEs were calculated using a density functional approach, including spin–orbit effects. During the calculation of the adiabatic ionization energies, the equilibrium geometries of the BeX<sub>2</sub><sup>+</sup> species were calculated; it was found that BeF<sub>2</sub><sup>+</sup> and BeCl<sub>2</sub><sup>+</sup> had bent equilibrium geometries (corresponding to the  $\tilde{X}^2B_2$  Renner–Teller component of the lowest  $^2\Pi_g$  state, in a linear configuration), whereas BeBr<sub>2</sub><sup>+</sup> and BeI<sub>2</sub><sup>+</sup> have linear ( $X^2\Pi_g$ ) equilibrium geometries. The calculated adiabatic ionization energies for BeF<sub>2</sub> and BeCl<sub>2</sub> are significantly higher than previously accepted values.

## I. Introduction

The geometries (linear or bent) of the group 2 (IIA) dihalides have been a matter of some interest for a number of years. In 1988, Hargittai published a summary of the known theoretical and experimental information regarding these molecules.<sup>1</sup> The general trend is that as the metal gets heavier or the halide gets lighter, then the more bent the molecule becomes. That some of the group IIA dihalides are bent is in disagreement with VSEPR theory and also simple Walsh diagrams in which only s and p orbitals are considered. Here we concentrate on the beryllium dihalides, which are widely agreed to be linear; however, there is little information on BeBr<sub>2</sub> and BeI<sub>2</sub>. In addition, the knowledge of the bond lengths and vibrational frequencies is far from complete.

**Experimental Background.** An early study by Akishin and Spiridonov<sup>2</sup> determined the bond lengths of all of the group IIA dihalides, except MgI<sub>2</sub> and the radioactive astatine compounds. All of the molecules were noted as being linear, but this is now known<sup>1</sup> not to be the case; clearly the quoted results must be treated with caution. The values obtained for the beryllium compounds were  $r = 1.40(3)$  Å for BeF<sub>2</sub>,  $1.75(2)$  Å for BeCl<sub>2</sub>,  $1.91(2)$  Å for BeBr<sub>2</sub>, and  $2.18(2)$  Å for BeI<sub>2</sub>, where in that work the measured  $r$  value will be an average over the thermally populated vibrational values.

BeF<sub>2</sub> was studied by Büchler and Klemperer;<sup>3</sup> they examined the vapor above heated BeF<sub>2</sub> and observed two infrared absorptions at 825 and 1520 cm<sup>-1</sup>, which they assigned to the bending and antisymmetric stretch modes, respectively. Matrix isolation studies, where two absorptions were observed at estimated gas-phase values of 345 and 1530 cm<sup>-1</sup>, were performed by Snelson.<sup>4,5</sup> The second vibration was assigned to the antisymmetric stretch ( $\omega_3$ ) and the former to the bend ( $\omega_2$ ). The 825 cm<sup>-1</sup> absorption of ref 3 was attributed by Snelson<sup>4</sup> as probably being due to a polymeric species in the gas phase. In 1991, Bernath and co-workers<sup>6</sup> performed Fourier transform infrared (FTIR) experiments on BeF<sub>2</sub> in the region of the antisymmetric stretch. They measured the fundamental as 1555.0479 cm<sup>-1</sup> and from this, assuming it to be the harmonic value, estimated the bending frequency at 347 cm<sup>-1</sup>. Analysis of the rotational structure allowed  $r_e$  to be derived as 1.372 917 0(95) cm<sup>-1</sup>; a recent electron diffraction study<sup>7</sup> obtains an estimate of  $r_e = 1.374(4)$  Å in agreement with the FTIR study. The latter study also derived vibrational frequencies, yielding  $\omega_1 = 594(60)$  cm<sup>-1</sup>,  $\omega_2 = 354(27)$  cm<sup>-1</sup>, and  $\omega_3 = 1519(90)$  cm<sup>-1</sup>.

BeCl<sub>2</sub> has been studied by infrared spectroscopy in the gas phase,<sup>3</sup> where  $\omega_2$  was measured as 482 cm<sup>-1</sup> and  $\omega_3$  was measured as 1113 cm<sup>-1</sup>. Matrix isolation infrared spectroscopy,<sup>4,5</sup> yielded estimated gas-phase values of  $\omega_2 = 250$  cm<sup>-1</sup> and  $\omega_3 = 1135$  cm<sup>-1</sup>;  $\omega_1$  was not observed but was estimated as 390 cm<sup>-1</sup>. Quite recently, an electron diffraction study<sup>8</sup> estimated  $r_e$  as 1.791(5) Å and derived  $\omega_1 = 346(29)$  cm<sup>-1</sup>,  $\omega_2 = 256(12)$  cm<sup>-1</sup>, and  $\omega_3 = 1219(73)$  cm<sup>-1</sup>. The value for  $\omega_2$  from ref 3 is clearly in error and may again be attributable to a

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polymeric species. There has also been a photoelectron spectrum of BeCl<sub>2</sub> reported.<sup>9</sup>

To the authors' knowledge, there is only one spectroscopic study of BeBr<sub>2</sub> and BeI<sub>2</sub>, namely, that of Snelson.<sup>5</sup> In that work,  $\omega_3$  was measured to be 1010 and 873 cm<sup>-1</sup> for BeBr<sub>2</sub> and BeI<sub>2</sub>, respectively;  $\omega_2$  was only measured for BeBr<sub>2</sub>, yielding 220 cm<sup>-1</sup>. The remaining three vibrational frequencies were estimated from force-field calculations, giving  $\omega_1(\text{BeBr}_2) = 230$  cm<sup>-1</sup>,  $\omega_1(\text{BeI}_2) = 160$  cm<sup>-1</sup>, and  $\omega_2(\text{BeI}_2) = 175$  cm<sup>-1</sup>.

**Theoretical Background.** Being closed-shell species, the group IIA dihalides have had some attention paid to them by theorists. Although considerable attention has been paid to some of these molecules, some have had very little attention indeed. The geometries (linear or bent) of some molecules have proven to be somewhat controversial, in particular CaF<sub>2</sub><sup>10–25</sup> where the best estimates appear to be  $\theta_e = 153–154^\circ$ .<sup>22,23</sup> The beryllium dihalides have been studied very little, with only BeF<sub>2</sub> receiving a significant amount of attention.

A number of Hartree–Fock studies<sup>26–30</sup> and a pseudopotential study<sup>21</sup> have been reported. A later calculation of the vibrational frequencies, where a triple- $\zeta$  plus polarization (two d functions) basis set was employed with the MP2 method, was performed by Dyke and Wright;<sup>16</sup> vibrational frequencies were calculated as  $\omega_1 = 728$  cm<sup>-1</sup>,  $\omega_2 = 338$  cm<sup>-1</sup>, and  $\omega_3 = 1573$  cm<sup>-1</sup>; these are obviously in good agreement with the recent experimental values noted above and confirm that the earlier value of  $\omega_2 = 825$  cm<sup>-1</sup> from ref 3 is spurious.  $r_e$  was calculated in ref 16 as 1.38 Å—in good agreement with the experimental value.<sup>6</sup> There are two other calculations at the MP2 level,<sup>31,32</sup> but they used smaller basis sets than ref 16: the first employed the 6-31G\* basis set, yielding  $r_e = 1.386$  Å and vibrational frequencies 735 cm<sup>-1</sup> ( $\omega_1$ ), 329 cm<sup>-1</sup> ( $\omega_2$ ), and 1622 cm<sup>-1</sup> ( $\omega_3$ ), while the second employed a DZV basis set, yielding  $r_e = 1.362$  Å and vibrational frequencies 769 cm<sup>-1</sup> ( $\omega_1$ ), 350 cm<sup>-1</sup> ( $\omega_2$ ), and 1686 cm<sup>-1</sup> ( $\omega_3$ ).

BeCl<sub>2</sub> has rather less attention paid to it, with HF calculations being reported.<sup>28–29</sup> A pseudopotential study<sup>21</sup> calculated the geometry and vibrational frequencies at the HF level of theory. The most reliable calculation until now was a MP2/6-31G\* calculation,<sup>31</sup> which yielded  $r_e = 1.787$  Å and vibrational frequencies 420 cm<sup>-1</sup> ( $\omega_1$ ), 234 cm<sup>-1</sup> ( $\omega_2$ ), and 1194 cm<sup>-1</sup> ( $\omega_3$ ).

An early ion-model calculation<sup>33</sup> concluded that BeBr<sub>2</sub> and BeI<sub>2</sub> would be linear (in agreement with the trends noted above and with ref 2). These conclusions were also confirmed in a pseudopotential study,<sup>21</sup> which calculated the geometries and vibrational frequencies; good agreement with available experimental values was obtained. Only the HF level of theory was used in that work,<sup>21</sup> and so it would be useful to confirm the results using correlated levels of theory.

The aim of the present work was initially to examine geometries and vibrational frequencies obtained using higher-level ab initio calculations on the two lightest BeX<sub>2</sub> species, to confirm that they are adequately described by these methods, and also to test the performance of the B3LYP density functional method on them. In addition, the harmonic vibrational frequencies for some of the modes enable previous estimates to be tested. For the first time, ab initio calculations are performed on the BeBr<sub>2</sub> and BeI<sub>2</sub> species using correlated levels of theory. For the latter two molecules, all-electron and effective core potentials (ECPs) are used, to confirm the latter are adequate for this species. Use of ECPs enables a good, flexible valence basis set to be used, which would otherwise become prohibitively expensive in the case of all-electron calculations. Finally, the cations of the BeX<sub>2</sub> species are studied, and adiabatic and

vertical ionization energies of the BeX<sub>2</sub> species are calculated. Comparison to the HeI photoelectron spectrum of BeCl<sub>2</sub> is made.

## II. Computational Details

Standard basis sets were used for Be, F, and Cl. For the all-electron calculations on BeBr<sub>2</sub>, the 6-31G\* basis set was used as the basic basis set, with further calculations being performed with the 6-311G basis set augmented with diffuse and polarization functions.<sup>34,35</sup> The calculations employed Møller–Plesset perturbation theory to second order (MP2) and the QCISD method. Density functional theory, in the form of B3LYP calculations, was also carried out by employing the basis sets mentioned above. The B3LYP method<sup>36</sup> uses a hybrid functional, which includes some Hartree–Fock exchange energy. For BeI<sub>2</sub>, all-electron calculations were only performed with the smaller 3-21G\* and 3-21+G\* basis sets (in the latter the diffuse sp function had an exponent of 0.038 33, which was derived by multiplying the most diffuse sp in the 3-21G\* basis set by <sup>1</sup>/<sub>3</sub>), again using the MP2, QCISD, and B3LYP methods.

For the ECP calculations on BeBr<sub>2</sub> and BeI<sub>2</sub>, the LANL2DZ ECP was used. Note that the LANL2DZ acronym usually implies the use of the Dunning double- $\zeta$  (D95) basis set<sup>37</sup> on the first row elements; however, in the present work the 6-31+G(2d) basis set was used for Be. To the LANL2DZ basis sets for Br and I were added one diffuse sp and two d polarization functions. For both bromine and iodine, the diffuse sp function had an exponent of 0.027, which was a factor of 5 smaller than the lowest p function exponent in the LANL2DZ basis set—this choice follows that of Chattaraj and Schleyer.<sup>38</sup> The d functions for bromine and iodine are taken from Schwerdtfeger et al.<sup>39</sup> and Glukhovtsev et al.,<sup>40</sup> and the exponents were as follows: Br, d (0.8, 0.2); I, d (0.5, 0.2). The basis sets for Br and I are identical with those used in our recent study<sup>41</sup> on BBr<sub>2</sub> and BI<sub>2</sub>, where augmenting the LANL2DZ basis set with the two d functions was found to be almost as accurate as adding a set of 3df functions. The basis set used can thus be denoted LANL2DZ + diffuse sp + 2d, which is simply denoted LAN in the following (where the LAN abbreviation also includes the use of the 6-31+G(2d) basis set for Be).

To gain a qualitative idea of the positions of the lowest-lying electronically excited states of the BeX<sub>2</sub> molecules, single-point CIS<sup>42</sup> calculations were performed.

For the vertical ionization energies, single-point calculations were performed. In the cases of BeF<sub>2</sub> and BeCl<sub>2</sub>, this geometry was that optimized at the MP2/6-311+G(3df) and MP2/6-311+G(2df) levels of theory, respectively. For BeBr<sub>2</sub> and BeI<sub>2</sub>, the geometry used was that at the QCISD/LAN level of theory. For BeF<sub>2</sub> and BeCl<sub>2</sub>, CASSCF+MRCI calculations were performed, where the active orbitals and electrons in the CAS were the valence ones. For the MRCI calculation, MOLPRO takes all important configurations from the CASSCF calculations to be the references in the subsequent MRCI. In the MRCI, the reference space is the same as that of the CAS, i.e., all valence molecular orbitals. All energies include the Davidson correction.<sup>43</sup> As an example, for the cationic <sup>2</sup>Σ<sup>+</sup> state of BeF<sub>2</sub><sup>+</sup>, the total number of uncontracted configurations was 311 million and that of the internally contracted configurations was 4.15 million (this is with the cc-pVTZ basis set for Be and the aug-cc-pVTZ basis set for F and is the largest CI of the four states considered). In addition, the RCCSD(T) method was employed: although this gives a nondegenerate wave function for the Π states, we have found in previous calculations that this problem does not greatly affect the accuracy of the results.<sup>44</sup> In addition, the results obtained here using the CASSCF+MRCI

**TABLE 1: Calculated Geometry and Vibrational Frequencies (cm<sup>-1</sup>) of BeF<sub>2</sub><sup>a</sup>**

| method                            | $r_e/\text{\AA}$ | $\omega_1(\sigma_g)$ | $\omega_2(\pi_u)$ | $\omega_3(\sigma_u)$ |
|-----------------------------------|------------------|----------------------|-------------------|----------------------|
| HF/6-311+G(3df)                   | 1.361            | 762.5 {1.39}         | 346.8 {0}         | 1648.8 {0}           |
| B3LYP/6-31G*                      | 1.380            | 742.3                | 309.5             | 1626.2               |
| MP2/6-31G* <sup>b</sup>           | 1.390            | 736.8                | 326.5             | 1621.3               |
| QCISD/6-31G*                      | 1.388            | 738.4                | 327.7             | 1625.3               |
| MP2/6-31+G*                       | 1.402            | 704.9                | 364.3             | 1541.4               |
| QCISD/6-311G(2d)                  | 1.379            | 733.2 [0]            | 357.2 [162]       | 1596.6 [340]         |
| B3LYP/6-311G(2df)                 | 1.376            | 729.4                | 337.4             | 1586.5               |
| MP2/6-311G(2df)                   | 1.382            | 721.9                | 325.9             | 1580.9               |
| MP2/6-311+G(3df)                  | 1.383            | 715.4 [0]            | 344.7 [168]       | 1555.1 [384]         |
| electron diffraction <sup>c</sup> | 1.40(3)          |                      |                   |                      |
| matrix isolation <sup>d</sup>     |                  | 680                  | 345               | 1555                 |
| electron diffraction <sup>e</sup> | 1.374(4)         | 594(60)              | 354(27)           | 1519(90)             |
| gas-phase FTIR <sup>f</sup>       | 1.3729710(95)    |                      | 347               | 1555.04              |

<sup>a</sup> Values in square brackets are infrared intensities (km mol<sup>-1</sup>); values in braces are Raman intensities (Å<sup>4</sup>/amu); values in italics were estimated. <sup>b</sup> These results are very similar to those obtained in ref 31, ostensibly at the same level of theory. <sup>c</sup> From ref 2. The  $r_e$  value was estimated. <sup>d</sup> From refs 4 and 5. The value for  $\omega_1$  was estimated. <sup>e</sup> From ref 7. Numbers in parentheses are errors in the last numbers. The  $r_e$  value was estimated. <sup>f</sup> From ref 6. Numbers in parentheses are errors in the last numbers. The value for  $\omega_2$  was estimated assuming the fundamental frequency for  $\nu_3$  was the harmonic value; the value given for  $\omega_3$  is the fundamental frequency.

and the RCCSD(T) approaches were comparable when the same basis set was used, but the RCCSD(T) calculations were ca. 2 orders of magnitude cheaper, therefore allowing the investigation of basis set saturation, which would have been impracticable using the CASSCF+MRCI approach. The basis sets used in the RCCSD(T) calculations were the (aug-)cc-pVXZ basis sets, X = T, Q, and 5; for the CASSCF+MRCI calculations, only the (aug-)cc-pVDZ and (aug-)cc-pVTZ basis sets were employed, and in the latter case, the f functions were omitted. Note that for Be only the cc-pVXZ basis sets were used, whereas for F and Cl the aug-cc-pVXZ basis sets were employed, owing to the larger electronegativity of these atoms.

Adiabatic ionization energies (AIEs) were calculated by optimizing the cation geometries at the UMP2, UB3LYP and UQCISD levels. Note that there is some question as to whether the BeX<sub>2</sub><sup>+</sup> cations are linear or bent, and so optimization was performed with and without a linear geometry constraint. Once the optimized geometry had been obtained, then single-point RCCSD(T) calculations were performed to obtain more reliable AIEs. The AIE is then simply obtained by the difference between the energies of the optimized geometries of the neutral and the cation, with correction for zero-point vibrational energy (ZPVE). Vertical ionization energies were calculated by the difference in energies of the cation and the neutral, at the optimized geometry of the neutral; no corrections for ZPVE have been made to these values.

All (U)HF, (U)MP2, (U)B3LYP, and (U)QCISD calculations employed the *Gaussian 94* suite of programs;<sup>45</sup> all CASSCF+MRCI and RCCSD(T) calculations employed MOLPRO.<sup>46</sup> Note that in the (U)MP2, (U)QCISD, and RCCSD(T) calculations the frozen core approximation was used. The ADF program<sup>47</sup> was used to calculate the vertical ionization energies of BeBr<sub>2</sub> and BeI<sub>2</sub> where relativistic and spin-orbit effects were included via the procedures outlined in ref 48; the (STO) basis sets used in these calculations were triple- $\zeta$  basis sets plus one set of polarization functions (TZP) and were performed at the QCISD/LAN-optimized geometry. The so-called 1/2-electron transition state method was employed to obtain the ionization energies.

### III. Results and Discussion

**(a) Geometries and Vibrational Frequencies.** The calculated results for BeF<sub>2</sub> are given in Table 1. As may be seen, there is good agreement between the calculated values. The variation of the calculated bond lengths and vibrational frequencies with the level of theory and basis set shows that the HF

method is inadequate to describe this species. In addition, small basis sets, such as 6-31G\*, are also inadequate. The role of the diffuse function is unclear: there is certainly a pronounced change on going from MP2/6-31G\* to MP2/6-31+G\*, but the change is less obvious when going from MP2/6-311G(2df) to MP2/6-311+G(3df)—this might imply that the diffuse function is just helping to fill in the inadequacies of the 6-31G\* basis set in the first case. The B3LYP method seems to be reliable for this species, and indeed the calculated properties are somewhat insensitive to the level of theory, once correlation past the MP2 level has been included. Our best estimate of  $r_e$  is  $1.380 \pm 0.005$  Å, which is in excellent agreement with the experimental values.

With regard to the vibrational frequencies, the general trend seems to be that, as the theoretical treatment becomes more complete, the stretch vibrational frequencies ( $\omega_1$  and  $\omega_3$ ) decrease in value, whereas the bending frequency ( $\omega_2$ ) increases. The “best” vibrational frequencies are in remarkably good agreement with the experimental values as far as  $\omega_2$  and  $\omega_3$  are concerned. (Note that, in general, the experimental results are vibrational energy level differences, whereas the calculated values are harmonic vibrational frequencies.) There have only been two experimental determinations of  $\omega_1$ —one was an estimate based on a simple force field model,<sup>4,5</sup> yielding 680 cm<sup>-1</sup>, and the other was obtained by fitting force constants to electron diffraction spectra,<sup>7</sup> yielding 594(60) cm<sup>-1</sup>. From the results presented here, given the close agreement for  $\omega_2$  and  $\omega_3$ , it seems clear that neither of these two values are particularly accurate, with the electron diffraction value being far too low and a value closer to 720 cm<sup>-1</sup> being more near to the true value: the matrix isolation estimate seems to be better than the fitted electron diffraction one. Our conclusions here are in line with those obtained by Kaupp et al.,<sup>21</sup> who used all-electron and pseudopotentials to study BeF<sub>2</sub> at the HF level, suggesting, perhaps, a fortuitous cancellation of errors in that work as no polarization functions appear to have been used on the halogen atoms and no correlation energy was included. The latter work obtained a vibrational frequency for  $\omega_1$  of 740–750 cm<sup>-1</sup>.

It is worth noting that in the FTIR study<sup>6</sup> some weak Q-branch features were found in the 1127–1235 cm<sup>-1</sup> range, which were suggested as arising from the  $\nu_1 + \nu_2$  combination band; however, this assignment led to the conclusion that  $\nu_1$  would be in the range 780–890 cm<sup>-1</sup>. The results here imply that the suggested assignment is incorrect and that  $\omega_1 = 720 \pm 10$  cm<sup>-1</sup>.



**TABLE 2: Calculated Geometry and Vibrational Frequencies of BeCl<sub>2</sub><sup>a</sup>**

| method                            | $r_e/\text{\AA}$ | $\omega_1(\sigma_g)$ | $\omega_2(\pi_u)$ | $\omega_3(\sigma_u)$ |
|-----------------------------------|------------------|----------------------|-------------------|----------------------|
| HF/6-311+G(3df)                   | 1.800            | 409.6 {4.73}         | 254.2 {0}         | 1155.5 {0}           |
| B3LYP/6-31G*                      | 1.802            | 400.9                | 233.9             | 1137.9               |
| MP2/6-31G* <sup>b</sup>           | 1.791            | 418.9                | 231.5             | 1187.7               |
| QCISD/6-31G*                      | 1.793            | 417.1                | 232.4             | 1180.8               |
| MP2/6-31+G*                       | 1.791            | 417.2                | 222.9             | 1181.0               |
| B3LYP/6-311G(2df)                 | 1.797            | 399.5                | 246.3             | 1128.8               |
| MP2/6-311G(2df)                   | 1.801            | 404.6 [0]            | 237.3 [51]        | 1150.4 [473]         |
| B3LYP/6-311+G(3df)                | 1.796            | 399.4 [0]            | 247.4 [45]        | 1129.9 [438]         |
| electron diffraction <sup>c</sup> | 1.75(2)          |                      |                   |                      |
| matrix isolation <sup>d</sup>     |                  | 390                  | 250               | 1135                 |
| electron diffraction <sup>e</sup> | 1.791(5)         | 346(29)              | 256(12)           | 1219(73)             |

<sup>a</sup> Values in square brackets are infrared intensities (km mol<sup>-1</sup>); values in braces are Raman intensities (Å<sup>4</sup>/amu); values in italics were estimated. <sup>b</sup> These results are very similar to those obtained in ref 31, ostensibly at the same level of theory. <sup>c</sup> From ref 2. The  $r_e$  value was estimated. <sup>d</sup> From refs 4 and 5. The value for  $\omega_1$  was estimated. <sup>e</sup> From ref 8. Numbers in parentheses are errors in the last numbers. The  $r_e$  value was estimated.

**TABLE 3: Calculated Geometry and Vibrational Frequencies for BeBr<sub>2</sub>**

| method                            | $r_e/\text{\AA}$ | $\omega_1(\sigma_g)$ | $\omega_2(\pi_u)$ | $\omega_3(\sigma_u)$ |
|-----------------------------------|------------------|----------------------|-------------------|----------------------|
| HF/6-311+G(3df)                   | 1.958            | 246.0 {3.63}         | 219.3 {0}         | 1013.2 {0}           |
| B3LYP/6-31G*                      | 1.918            | 252.1                | 355.5             | 1083.7               |
| MP2/6-31G*                        | 1.922            | 255.1                | 355.7             | 1096.9               |
| MP2/6-31+G*                       | 1.942            | 245.4                | 311.3             | 1048.1               |
| B3LYP/LAN <sup>b</sup>            | 1.968            | 237.3                | 208.3             | 983.7                |
| MP2/LAN <sup>b</sup>              | 1.967            | 242.2                | 218.0             | 1003.3               |
| QCISD/LAN <sup>b</sup>            | 1.968            | 240.8 [0]            | 219.9 [27]        | 996.3 [407]          |
| B3LYP/6-311G(2df)                 | 1.949            | 242.0                | 217.6             | 1001.7               |
| B3LYP/6-311+G(3df)                | 1.950            | 241.7 [0]            | 213.7 [25]        | 1000.7 [399]         |
| electron diffraction <sup>c</sup> | 1.91(2)          |                      |                   |                      |
| matrix isolation <sup>d</sup>     |                  | 230                  | 220               | 1010                 |

<sup>a</sup> Values in square brackets are infrared intensities (km mol<sup>-1</sup>); values in braces are Raman intensities (Å<sup>4</sup>/amu); values in italics were estimated. <sup>b</sup> LAN represents the LANL2DZ + diff sp + 2d basis set; see text for details. <sup>c</sup> From ref 2. The  $r_e$  value was estimated. <sup>d</sup> From ref 5. The value for  $\omega_1$  was estimated.

For BeCl<sub>2</sub>, similarly good agreement is obtained for  $\omega_2$  and  $\omega_3$ , where close agreement with the matrix isolation results of Snelson<sup>4,5</sup> are obtained (Table 2). For  $\omega_1$ , an estimate from simple force field considerations<sup>4,5</sup> leads to a value in very good agreement with our calculated value of  $\omega_1$  (400 ± 10 cm<sup>-1</sup>). As with BeF<sub>2</sub>, poorer agreement is found between the fitted electron diffraction values<sup>8</sup> and the best calculated values. The bond length obtained from the MP2/6-311G(2df) calculation is in very good agreement with the electron diffraction studies;<sup>2,8</sup> seeing the good agreement between these two methods and the FTIR study<sup>6</sup> for BeF<sub>2</sub> implies that the value of  $r_e$  for BeCl<sub>2</sub> is 1.800 ± 0.005 Å. The good agreement between calculated and experimental results, even with the smaller basis sets, seems to suggest that the 6-31G\* basis set is adequate for BeCl<sub>2</sub> while it was not for BeF<sub>2</sub>. As with BeF<sub>2</sub>, good agreement with the all-electron and pseudopotential results of ref 21 is obtained.

For BeBr<sub>2</sub>, again matrix isolation studies<sup>5</sup> have yielded two vibrational frequencies ( $\omega_2$  and  $\omega_3$ ), which agree well with the calculated values here (see Table 3). In comparison to BeF<sub>2</sub> and BeCl<sub>2</sub>, the basis set requirements for a reliable calculation of the vibrational frequencies are more stringent, with the results using the 6-31G basis sets being in much poorer agreement with experiment than those obtained using the 6-311G ones. Of note is that the basis sets based on the LANL2 ECP are performing well, giving calculated values in excellent agreement with the all-electron calculations, even when the B3LYP method is employed; in fact, the HF, MP2, QCISD, and B3LYP calculated

**TABLE 4: Calculated Geometry and Vibrational Frequencies for BeI<sub>2</sub>**

| method                            | $r_e/\text{\AA}$ | $\omega_1(\sigma_g)$ | $\omega_2(\pi_u)$ | $\omega_3(\sigma_u)$ |
|-----------------------------------|------------------|----------------------|-------------------|----------------------|
| HF/3-21G*                         | 2.196            | 173.6 {3.22}         | 199.2 {0}         | 1031.5 {0}           |
| B3LYP/3-21G*                      | 2.179            | 174.0                | 163.4             | 920.9                |
| MP2/3-21G*                        | 2.191            | 175.4                | 151.2             | 925.6                |
| QCISD/3-21G*                      | 2.196            | 173.5                | 149.5             | 915.7                |
| MP2/3-21+G*                       | 2.192            | 173.5                | 149.5             | 915.7                |
| B3LYP/LAN <sup>b</sup>            | 2.170            | 168.1                | 182.3             | 876.7                |
| MP2/LAN <sup>b</sup>              | 2.167            | 172.5                | 185.6             | 899.2                |
| QCISD/LAN <sup>b</sup>            | 2.173            | 170.5 [0]            | 187.6 [13]        | 887.5 [412]          |
| electron diffraction <sup>c</sup> | 2.18(2)          |                      |                   |                      |
| matrix isolation <sup>d</sup>     |                  | 160                  | 175               | 873                  |

<sup>a</sup> Values in square brackets are infrared intensities (km mol<sup>-1</sup>); values in braces are Raman intensities (Å<sup>4</sup>/amu); values in italics were estimated. <sup>b</sup> LAN represents the LANL2DZ + diff sp + 2d basis set; see text for details. <sup>c</sup> From ref 2. The  $r_e$  value was estimated. <sup>d</sup> From ref 5. The values for  $\omega_1$  and  $\omega_2$  were estimated.

values are all in fairly good agreement. The combination of density functional theory with ECPs, as pointed out previously,<sup>41</sup> thus makes a powerful tool for accurate calculation of properties, as long as the valence part of the basis set is well designed. The estimated value<sup>5</sup> of  $\omega_1$  is in good agreement with the calculated values here—we quote a value of 240 ± 10 cm<sup>-1</sup> based on our results. The calculated bond length is in good agreement with the early electron diffraction results<sup>2</sup> but slightly longer; we quote  $r_e = 1.95 \pm 0.02$  Å as our best estimate. The only other calculation of the geometry and vibrational frequencies of BeBr<sub>2</sub> is that of Kaupp et al.,<sup>21</sup> who used a pseudopotential approach at the HF level of theory. They obtained  $r_e = 1.96$ – $1.97$  Å but thought that electron correlation would make that value increase, whereas the value obtained here is a slightly shorter value; our results suggest that the basis set as well as electron correlation is important. Generally, considering that only the HF approach was used, the calculated harmonic vibrational frequencies in ref 21 are in remarkably good agreement with those obtained here.

For BeI<sub>2</sub>, only small basis sets were used for the all-electron calculations; however, it was possible to use a larger valence basis set when the LANL2 ECP was employed. As may be seen from Table 4, the basis set requirements are still quite important here. Our best values are the QCISD/LAN values. For the vibrational frequencies, these are expected to be very close to the experimental values, by comparison with the BeBr<sub>2</sub> results, and indeed the experimental value<sup>5</sup> for  $\omega_3$  concurs with this. Only estimated values are available for  $\omega_1$  and  $\omega_2$ , but these agree very well with the calculated values, and we cite  $\omega_1 = 170 \pm 10$  cm<sup>-1</sup> and  $\omega_2 = 185 \pm 10$  cm<sup>-1</sup>. As with BeBr<sub>2</sub>, the calculated bond length is in good agreement with the early electron diffraction thermally averaged results;<sup>2</sup> our best estimate is 2.17 ± 0.02 Å, which includes that previous value. Compared to the pseudopotential results of ref 21, a good agreement with the harmonic vibrational frequencies and also the calculated  $r_e$  value (2.19–2.20 Å) is obtained.

Finally we note that the calculated infrared intensities are very similar throughout the series, with the  $\omega_1$  intensity being zero, owing to it being symmetry forbidden and  $\omega_3$  being much more intense than  $\omega_2$ ; the latter is apparently in contrast to the matrix isolation infrared results of Snelson,<sup>5</sup> in which the intensities of  $\omega_2$  and  $\omega_3$  appear to be very similar, although the  $\omega_3$  band may be off scale; no indication as to the relative intensity is given in the text of that paper. Although no Raman spectrum has been recorded,  $\omega_1$  is the only Raman active mode (as may be seen from symmetry or more directly via the mutual exclusion principle between infrared and Raman spectra for a

centrosymmetric molecule)—this is confirmed from calculated Raman intensities at the HF level.

**(b) Electronically Excited States.** To ascertain a qualitative picture of the excited electronic states of the  $\text{BeX}_2$  molecules, single-point CIS calculations were performed. Although the CIS method is known not to be highly accurate, it is adequate for the picture required here. The CIS calculations performed were the following: CIS/6-311+G(2d)//MP2/6-311+G(3df) [ $\text{BeF}_2$ ]; CIS/6-311+G(2d)//B3LYP/6-311+G(3df) [ $\text{BeCl}_2$ ]; CIS/6-311+G(2d)//B3LYP/6-311G(2df) [ $\text{BeBr}_2$ ]; and CIS/LAN//QCISD/LAN [ $\text{BeI}_2$ ]. The outer electronic configuration was calculated to be  $\dots\sigma_u^2\sigma_g^2\pi_u^4\pi_g^4$  for  $\text{BeF}_2$  but  $\dots\sigma_g^2\sigma_u^2\pi_u^4\pi_g^4$  for the other three molecules. The results of these calculations showed that the lowest singlet electronically excited-state arises from a  $\sigma_g \leftarrow \pi_g$  (LUMO  $\leftarrow$  HOMO) in all cases, with the transition energies calculated to be 11.8, 8.8, 7.9, and 6.8 eV for  $\text{BeX}_2$  ( $X = \text{F, Cl, Br, and I, respectively}$ ). This transition is, however, dipole forbidden. The lowest dipole-allowed transition in each case corresponded to a  $\sigma_g \leftarrow \pi_u$  transition, involving the highest-occupied  $\pi_u$  orbital and the LUMO; the energy of this transition was calculated to be 12.5, 9.2, 8.1, and 7.4 eV for  $\text{BeX}_2$  ( $X = \text{F, Cl, Br, and I, respectively}$ ).

The conclusion is that laser-based diagnostics involving electronic spectroscopy will not be straightforward to use for these species, although multiphoton techniques may be possible.

**(c) Relativistic Effects on the Geometry.** An extension of the G2 method has been formulated by Glukhovtsev et al. to study bromine- and iodine-containing molecules.<sup>40</sup> In that work, they compared results using relativistic and nonrelativistic ECPs and nonrelativistic all-electron calculations. Their conclusion was that relativistic effects were not affecting the calculated properties. As it happens, the 6-311G basis set and the ECP potential for bromine are both nonrelativistic, whereas the iodine ECP has relativistic effects included. Pyykkö<sup>49</sup> has summarized the effects of relativity on molecular geometries, and the trend noted was for bond lengths to get shorter when relativistic effects are included. Thus, the calculated beryllium dibromide bond lengths may be slightly too long, although relativistic effects should not be of too much importance. (It should be noted, however, that a recent paper on the interhalogens<sup>50</sup> concluded that the bonding got weaker when relativistic effects were included; i.e., the bond lengths got longer and the harmonic frequencies decreased.) The effect of relativity on bond angles is not yet known.<sup>49</sup>

**(d) Ionization Energies.** The photoelectron spectra of some group IIA dihalides were initially studied by Hammer et al.,<sup>51</sup> but a lack of structure did not allow the measurement of any detailed ionization energies. Later, Lee and Potts<sup>9</sup> recorded photoelectron spectra of a number of group IIA dihalides, and among them was  $\text{BeCl}_2$ . The spectrum showed four structureless bands, which were assigned to the four lowest-lying electronic states:  $X^2\Pi_g$ ,  $A^2\Pi_u$ ,  $B^2\Sigma_u^+$ , and  $C^2\Sigma_g^+$  on the basis of HF calculations. This paper<sup>9</sup> has been cited on the NIST Webbook page,<sup>52</sup> and in the GIANT tables,<sup>53</sup> but the cited data are incorrect. First, the adiabatic ionization energy is cited as 11.15 eV—it is not clear where this value comes from, because it is not cited in ref 9, but it may have been simply measured from the spectrum.<sup>54</sup> In addition, the vertical ionization energy (VIE) for the  $X^2\Pi_g$  state is cited in ref 52 as 12.75 eV—this appears to have been taken from Table 6 of ref 9, which is not the actual measured VIE, but a derived value; the correct value for the VIE of the  $X^2\Pi_g$  state is given in Table 5 of ref 9 as  $12.36 \pm 0.02$  eV. Finally, the appearance potential of  $\text{BeCl}_2$  has been measured in electron impact studies, and values of  $12.5 \pm 1$

eV<sup>55</sup> and  $12.6 \pm 0.4/12.4 \pm 0.4$  eV<sup>56</sup> were obtained. It is clear that there is some uncertainty as to what the AIE and VIE of  $\text{BeCl}_2$  are.

For  $\text{BeF}_2$ , no photoelectron spectrum has yet been recorded, but the ionization energy has been obtained from appearance potentials in three electron impact mass spectrometric experiments as  $14.5 \pm 1$ ,<sup>55</sup>  $14.7 \pm 0.4$ ,<sup>57</sup> and  $14.8 \pm 0.4/14.5 \pm 0.4$  eV,<sup>58</sup> with a recommended value of  $14.6 \pm 0.5$  eV being cited in ref 53.

No ionization energies appear to be available for  $\text{BeBr}_2$  or  $\text{BeI}_2$ .

The ground-state  $\text{BeX}_2^+$  cations are interesting because they are subject to the Renner–Teller interaction and so may distort away from the linear geometry. Indeed, for  $\text{BeF}_2^+$  there have been three theoretical studies,<sup>59–61</sup> which have shown that indeed the minimum-energy geometry associated with the lowest  $^2\Pi_g$  state is actually a bent  $\tilde{X}^2B_2$  state, which arises as the degeneracy of the  $^2\Pi_g$  state is lost upon bending. In the earlier two studies,<sup>59,60</sup> a secondary minimum was found at  $180^\circ$ , but it was noted<sup>60</sup> that this might be an artifact of the low levels of theory used (UHF calculations in ref 59 and equation of motion/propagator calculations in ref 60). Indeed in the most recent MCSCF study,<sup>61</sup> this minimum disappears, leaving only one minimum on the  $^2B_2$  surface at  $96^\circ$ . The bent well was  $1345 \text{ cm}^{-1}$  below that of the linear conformation, suggesting that this will be a static minimum.

Here we initially aim to calculate the VIEs using high levels of theory [CCSD(T) and CASSCF+MRCI]. (Note that relativistic effects have been found to have a variable effect on the accuracy of ionization energies.<sup>62</sup>) After that, the geometry of the  $\text{BeX}_2^+$  species were optimized and AIEs calculated. Because the outermost orbital for all four  $\text{BeX}_2$  species is a nonbonding  $\pi_g$  orbital, it is expected that the first AIEs and VIEs should be very similar; however, it may be that the possible change in geometry caused by a distortion to a bent geometry by the Renner–Teller effect could separate these two quantities.

**(i) Vertical Ionization Energies.  $\text{BeCl}_2$ .** First we shall consider  $\text{BeCl}_2$ , on the grounds that the photoelectron spectrum (and so the VIEs) are available. Taking the VIE values from Table 5 of ref 9 (which are the actual experimental measurements),<sup>63</sup> the numbers are  $12.36 \pm 0.02$  eV ( $X^2\Pi_g$ ),  $13.13 \pm 0.02$  eV ( $A^2\Pi_u$ ),  $14.26 \pm 0.04$  eV ( $B^2\Sigma_u^+$ ), and  $14.89 \pm 0.04$  eV ( $C^2\Sigma_g^+$ ). As may be seen from Table 5 in the present work, the calculated VIEs are converging as the basis set increases, which suggests that the values at the highest level of theory should be close to the true values. When compared to the experimental values, the agreement is extremely pleasing and confirms the assignment of the spectrum. Given that the vibrational structure was unresolved in the photoelectron spectrum, then it is possible that the actual VIE could be slightly different from that reported.

**$\text{BeF}_2$ .** The calculated VIEs for  $\text{BeF}_2$  are given in Table 6, as may be seen, convergence with increasing basis set size is also obtained, as for  $\text{BeCl}_2$ . As noted above, there is no photoelectron spectrum of  $\text{BeF}_2$ . Of note is that the  $^2\Sigma_g^+$  state is below the  $^2\Sigma_u^+$  state—i.e., the other way around compared to  $\text{BeCl}_2$  and the two heavier dihalides (see below). Interestingly, for  $\text{MgF}_2^+$ , the  $^2\Sigma_g^+$  state was calculated to lie higher than the  $^2\Sigma_u^+$  state.<sup>64</sup>

**$\text{BeBr}_2$  and  $\text{BeI}_2$ .** For  $\text{BeBr}_2$  and  $\text{BeI}_2$ , the calculated VIEs are given in Tables 7 and 8, respectively. Note now that, owing to the heavy halide atoms, spin–orbit effects must be taken into account. The calculated VIEs indicate that it ought to be possible to see the splitting of the two  $\Pi$  states in a photoelectron spectrum, if the resolution is reasonable; some splitting was seen

**TABLE 5: Calculated Vertical Ionization Energies (eV) for BeCl<sub>2</sub> (See Text for Details)<sup>a</sup>**

| method                       | <sup>2</sup> Π <sub>g</sub> | <sup>2</sup> Π <sub>u</sub> | <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> | <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> |
|------------------------------|-----------------------------|-----------------------------|--|--|
| CASSCF+MRCI/aug-cc-pVDZ      | 12.18                       |                             |  |  |
| CASSCF+MRCI/aug-cc-pVTZ      | 12.14                       |                             |  |  |
| CCSD(T)/aug-cc-pVTZ(spdl)    | 12.22                       | 12.88                       | 14.15                                    | 14.65                                    |
| CCSD(T)/aug-cc-pVQZ(spdl)    | 12.21                       | 12.87                       | 14.14                                    | 14.65                                    |
| CCSD(T)/aug-cc-pVQZ(spdlf)   | 12.37                       | 13.01                       | 14.23                                    | 14.73                                    |
| CCSD(T)/aug-cc-pVQZ(spdlfg)  | 12.47                       | 13.12                       | 14.33                                    | 14.82                                    |
| CCSD(T)/aug-cc-pV5Z(spdlfgh) | 12.50                       | 13.14                       | 14.36                                    | 14.87                                    |
| experimental <sup>b</sup>    | 12.36 ± 0.02                | 13.13 ± 0.02                | 14.26 ± 0.04                             | 14.89 ± 0.04                             |

<sup>a</sup> Note that no zero-point vibrational energy corrections have been made. <sup>b</sup> From photoelectron spectra (ref 9).

**TABLE 6: Calculated Vertical Ionization Energies (eV) for BeF<sub>2</sub> (See Text for Details)<sup>a</sup>**

| method                      | <sup>2</sup> Π <sub>g</sub> | <sup>2</sup> Π <sub>u</sub> | <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> | <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> |
|-----------------------------|-----------------------------|-----------------------------|--|--|
| CASSCF+MRCI/aug-cc-pVDZ     | 15.34                       | 16.06                       | 17.02                                    | 17.17                                    |
| CASSCF+MRCI/aug-cc-pVTZ     | 15.08                       | 15.79                       | 16.68                                    | 16.90                                    |
| CCSD(T)/aug-cc-pVQZ(spdl)   | 15.52                       | 16.21                       | 17.20                                    | 17.41                                    |
| CCSD(T)/aug-cc-pVQZ(spdlf)  | 15.62                       | 16.32                       | 17.25                                    | 17.48                                    |
| CCSD(T)/aug-cc-pVQZ(spdlfg) | 15.69                       | 16.38                       | 17.32                                    | 17.54                                    |

<sup>a</sup> Note that no zero-point vibrational energy corrections have been made.

**TABLE 7: Calculated Ionization Energies of BeBr<sub>2</sub> (See Text for Details)<sup>a</sup>**

| cationic <i>j</i> state | L–S equivalent                              | VIE/eV |
|-------------------------|---|--------|
| 3/2 <sub>g</sub>        | <sup>2</sup> Π <sub>3/2g</sub>              | 10.63  |
| 1/2 <sub>g</sub>        | <sup>2</sup> Π <sub>1/2g</sub>              | 10.97  |
| 3/2 <sub>u</sub>        | <sup>2</sup> Π <sub>3/2u</sub>              | 11.08  |
| 1/2 <sub>u</sub>        | <sup>2</sup> Π <sub>1/2u</sub>              | 11.35  |
| 1/2 <sub>u</sub>        | <sup>2</sup> Σ <sub>1/2u</sub> <sup>+</sup> | 12.88  |
| 1/2 <sub>g</sub>        | <sup>2</sup> Σ <sub>1/2g</sub> <sup>+</sup> | 13.47  |

<sup>a</sup> Note that no zero-point vibrational energy corrections have been made.

**TABLE 8: Calculated Vertical Ionization Energies of BeI<sub>2</sub> (See Text for Details)<sup>a</sup>**

| cationic <i>j</i> state | L–S equivalent                              | VIE/eV |
|-------------------------|---|--------|
| 3/2 <sub>g</sub>        | <sup>2</sup> Π <sub>3/2g</sub>              | 9.39   |
| 1/2 <sub>g</sub>        | <sup>2</sup> Π <sub>1/2g</sub>              | 10.00  |
| 3/2 <sub>u</sub>        | <sup>2</sup> Π <sub>3/2u</sub>              | 9.89   |
| 1/2 <sub>u</sub>        | <sup>2</sup> Π <sub>1/2u</sub>              | 10.31  |
| 1/2 <sub>u</sub>        | <sup>2</sup> Σ <sub>1/2u</sub> <sup>+</sup> | 11.77  |
| 1/2 <sub>g</sub>        | <sup>2</sup> Σ <sub>1/2g</sub> <sup>+</sup> | 12.48  |

<sup>a</sup> Note that no zero-point vibrational energy corrections have been made.

**TABLE 9: Calculated Equilibrium Geometry for BeF<sub>2</sub><sup>+</sup>**

| method                   | <i>r</i> <sub>e</sub> /Å | θ/deg | ω <sub>1</sub> /cm <sup>−1</sup> | ω <sub>2</sub> /cm <sup>−1</sup> | ω <sub>3</sub> /cm <sup>−1</sup> <sup>a</sup> |
|--------------------------|--------------------------|-------|----------------------------------|----------------------------------|---|
| UB3LYP/6-311+G*          | 1.425                    | 107.7 | 993                              | 132                              | 921   |
| ⟨S <sup>2</sup> ⟩ = 0.76 |                          |       |                                  |                                  |   |
| UMP2/6-311+G(2d)         | 1.436                    | 90.8  | 1087                             | 327                              | 2514  |
| ⟨S <sup>2</sup> ⟩ = 0.79 |                          |       |                                  |                                  |   |
| UQCISD/6-311+G(2d)       | 1.434                    | 93.7  | 1063                             | 280                              | 584   |
| ⟨S <sup>2</sup> ⟩ = 0.79 |                          |       |                                  |                                  |   |

<sup>a</sup> Note that the ω<sub>3</sub> values are unreliable.

in the photoelectron spectra of the other group IIA bromides and iodides.<sup>9</sup>

(ii) *Equilibrium Geometries of the BeX<sub>2</sub><sup>+</sup> Species and Adiabatic Ionization Energies.* BeF<sub>2</sub><sup>+</sup>. The calculated equilibrium geometry of BeF<sub>2</sub><sup>+</sup> is given in Table 9; as may be seen, the molecule is calculated to be bent at all levels of theory, with three real frequencies indicating a minimum-energy structure (note that the ω<sub>3</sub> value is unreliable). When a linear constraint was applied, then imaginary frequencies were calculated for one of the π bending vibrations at the UMP2 and UQCISD levels

**TABLE 10: Calculated Equilibrium Geometry for BeCl<sub>2</sub><sup>+</sup>**

| method                   | <i>r</i> <sub>e</sub> /Å | θ/deg | ω <sub>1</sub> /cm <sup>−1</sup> | ω <sub>2</sub> /cm <sup>−1</sup> | ω <sub>3</sub> /cm <sup>−1</sup> <sup>a</sup> |
|--------------------------|--------------------------|-------|----------------------------------|----------------------------------|---|
| UB3LYP/6-311+G(3df)      | 1.831                    | 180   |                                  |                                  |   |
| ⟨S <sup>2</sup> ⟩ = 0.76 |                          |       |                                  |                                  |   |
| UMP2/6-311G(2d)          | 1.827                    | 111.1 | 693                              | 102                              | 2511  |
| ⟨S <sup>2</sup> ⟩ = 0.79 |                          |       |                                  |                                  |   |
| UQCISD/6-311+G(2d)       | 1.434                    | 93.7  | 621                              | 58                               | 611   |
| ⟨S <sup>2</sup> ⟩ = 0.80 |                          |       |                                  |                                  |   |

<sup>a</sup> Note that the ω<sub>3</sub> values are unreliable.

(these vibrations are not calculated to be degenerate, owing to the use of unrestricted wave functions), suggesting a transition state; the UB3LYP method apparently led to a minimum at both a bent and a linear geometry, but the linear minimum is thought to be an artifact, because UHF wave functions lead to such a spurious minimum.<sup>59–61</sup> Note that spin contamination was small, with ⟨S<sup>2</sup>⟩ < 0.8. RCCSD(T) calculations (cc-pVQZ basis set for Be and aug-cc-pVQZ basis set for F) were then performed at the UMP2/6-311+G(2d)-optimized geometry for the  $\tilde{X}^2B_2$  state and the MP2/6-311+G(3df)-optimized geometry of the  $X^1\Sigma_g^+$  state to calculate the AIE: the calculated value was 15.26 eV. The calculation of the vibrational frequencies for the cation was hampered by the use of UHF wave functions, which led to some spurious values for ω<sub>3</sub> (see Table 9); however, the correction for ZPVE should not exceed 0.05 eV, and so a value of AIE-(BeF<sub>2</sub>) = 15.3 ± 0.2 eV would seem to be reasonable, where the probably generous error covers the correction for ZPVE, and the estimated error in the RCCSD(T) energies calculated, as surmised from the accuracy of the BeCl<sub>2</sub> VIEs when compared to experiment. This value compares with the literature value<sup>53</sup> of 14.6 ± 0.5 eV, which was based on early mass spectrometric experiments.<sup>55,57,58</sup>

Finally, we note that at the UB3LYP/6-311+G(3df) level of theory the energy difference between the (fully optimized) <sup>2</sup>Π<sub>g</sub> linear geometry of BeF<sub>2</sub><sup>+</sup> and the bent  $\tilde{X}^2B_2$  one was only 29.3 cm<sup>−1</sup> but that, at the UMP2/6-311+G(2d) and UQCISD/6-311+G(2d) levels, this difference was 2400 and 1900 cm<sup>−1</sup>—the latter two values agree much better with the corresponding value from the MCSCF study<sup>61</sup> of 1345 cm<sup>−1</sup>. Our best estimate comes, however, from the difference between the VIE and the AIE calculated at the RCCSD(T) level of theory, yielding 3500 cm<sup>−1</sup>, which is significantly higher and about 4 times higher than the corresponding value for BeCl<sub>2</sub><sup>+</sup>. We conclude that the UB3LYP method is not able to cope with the cation.

BeCl<sub>2</sub>. The calculated optimized geometry for BeCl<sub>2</sub><sup>+</sup> is given in Table 10; as may be seen, it is calculated to be linear at the UB3LYP level but bent at the UMP2 and UQCISD levels, with three real frequencies in the latter case indicating a minimum-energy structure. Unfortunately, when the linear constraint was applied, then although the geometry optimized successfully the vibrational frequencies contained some unrealistic values, and so it is not possible to say whether a minimum or a saddle point is obtained. Hence, it appears BeCl<sub>2</sub><sup>+</sup> is bent, but with a low



barrier to linearity (vide infra). RCCSD(T) calculations (cc-pVQZ basis set for Be and aug-cc-pVQZ basis set for Cl) were then performed at the UMP2/6-311+G(2d)-optimized geometry of the  $\tilde{X}^2B_2$  state and the MP2/6-311G(2df)-optimized geometry of the  $X^1\Sigma_g^+$  state to calculate the AIE: the calculated value was 12.39 eV. Note that spin contamination was small in all cases, with  $\langle S^2 \rangle \leq 0.8$ . The calculation of the vibrational frequencies for the cation was hampered by the use of UHF wave functions, which led to some unrealistic values; however, the correction for the zero-point energy should not exceed 0.05 eV, and so a value  $AIE(BeCl_2) = 12.4 \pm 0.2$  eV would seem reasonable (where the error covers the correction for ZPVE, and the estimated error in the RCCSD(T) energies calculated, as surmised from the accuracy of the VIEs when compared to experiment). This value compares very well with the values obtained in the electron impact studies<sup>55,56</sup> but very poorly with the recommended value of 11.15 eV.<sup>52,53</sup> As noted above, the latter value appears to have been taken from the onset of the photoelectron spectrum presented in ref 9, and it would appear that this onset is too low, perhaps because of hot vibrational bands or because of instrumental effects.

The barrier to linearity may be obtained at the RCCSD(T) level as the difference between the calculated VIE and AIE, yielding  $900\text{ cm}^{-1}$ .

**BeBr<sub>2</sub> and BeI<sub>2</sub>.** When the UMP2, UB3LYP, and UQCISD methods were used to optimize the geometries of the ground state of BeBr<sub>2</sub><sup>+</sup> and BeI<sub>2</sub><sup>+</sup>, starting at a bent geometry (90°), linearity was always reached. Because BeCl<sub>2</sub><sup>+</sup> had a much smaller barrier to linearity than BeF<sub>2</sub><sup>+</sup>, then this trend is not surprising. One way of viewing this is that the Renner–Teller interaction (which may be interpreted as a quenching of the orbital angular momentum of the  $X^2\Pi_g$  state) is unable to quench the larger spin–orbit angular momentum in the heavier beryllium dihalide cations, but it can for the lighter ones. At the highest levels of theory, QCISD/LAN, the bond lengths were calculated to be 1.990 Å (BeBr<sub>2</sub><sup>+</sup>) and 2.184 Å (BeI<sub>2</sub><sup>+</sup>). Again, some spurious values for the antisymmetric stretch vibrational frequency were obtained.

It is not as straightforward to obtain the AIEs to the linear BeBr<sub>2</sub><sup>+</sup> and BeI<sub>2</sub><sup>+</sup> cations using the ADF code. We note, however, that the AIEs calculated for BeBr<sub>2</sub><sup>+</sup> at the (U)B3LYP/6-31G\*, (U)MP2/6-31G\*, (U)B3LYP/6-311G(2df), and (U)QCISD/LAN levels were 10.84, 11.18, 10.90, and 11.14 eV, respectively, which leads us to suggest a value of  $11.2 \pm 0.5$  eV, where the error is estimated. For BeI<sub>2</sub>, the AIE was calculated to be 9.83, 10.07, and 10.01 eV at the (U)B3LYP/LAN, (U)MP2/LAN, and (U)QCISD/LAN levels, which leads to an estimated AIE of  $10.0 \pm 0.5$  eV. Note that spin–orbit coupling needs to be considered here. As an estimate we take the values obtained from the ADF code for the VIEs—this suggests that the spin–orbit coupling is 0.34 eV for BeBr<sub>2</sub><sup>+</sup> and 0.61 eV for BeI<sub>2</sub><sup>+</sup>. The latter suggests that the lowest ionization energy corresponding to the process  $BeX_2^+(3/2_g) \leftarrow BeX_2(X^1\Sigma_g^+)$  is  $11.0 \pm 0.5$  eV for X = Br and  $9.7 \pm 0.5$  eV for X = I.

#### IV. Conclusions and General Remarks

Unlike other group IIA dihalides, the beryllium dihalides are all linear and so conform to expectations based on the VSEPR theory or simple Walsh diagrams. The preference of a group IIA dihalide for a bent structure is thought to be due to the involvement of d orbitals in the bonding (indeed modified Walsh diagrams,<sup>11</sup> where account of d orbital involvement is taken, do predict bent equilibrium structures). The linearity of the

beryllium dihalides can probably most easily be attributed to the absence of low-lying d orbitals on the beryllium atom.

The results here suggest that the bond length gets gradually longer as the mass of the halide increases, as expected from the increasing size of the halide moiety. In addition, the vibrational frequencies gradually get smaller as the halide increases in mass, as expected. A complete set of bond lengths and vibrational frequencies are presented for all of the BeX<sub>2</sub> species, except for the BeAt<sub>2</sub> species, which is unlikely to be observed. Very good agreement is obtained between the calculated values here and the available experimental data; in addition, good agreement with the results obtained in a previous HF plus pseudopotential study was obtained. It appears that these species are not particularly demanding as far as ab initio calculations are concerned, but a reasonable valence basis set is required. Of note is that the simple force field model, used by Snelson<sup>4,5</sup> to estimate unobserved vibrational frequencies for these compounds, performed extremely well for these species. The authors of ref 6 noted in regard to BeF<sub>2</sub> that it would be useful to record the Raman spectrum to observe the  $\omega_1$  vibrational mode—we reiterate this sentiment with regard to all of the species but expect that the observed values will not be too different from those obtained in the present work.

We have shown that the lowest available excited electronic state formed from a single excitation is dipole forbidden but that there are allowed transitions to higher energy; the allowed states appear to be rather high for standard laser-based detection methods.

VIEs and AIEs are calculated. Experimentally, only VIEs for BeCl<sub>2</sub> are known, and the agreement with those is very good, giving us confidence that the other calculated values are reliable. The calculated AIEs for BeF<sub>2</sub> and BeCl<sub>2</sub> are much higher than the presently accepted values, although for BeCl<sub>2</sub> good agreement is found with early electron impact values. Clearly, this needs to be investigated. Finally, the equilibrium geometries of the BeX<sub>2</sub><sup>+</sup> species were calculated: BeF<sub>2</sub><sup>+</sup> and BeCl<sub>2</sub><sup>+</sup> were found to have bent  $\tilde{X}^2B_2$  ground states, which is the lower component of the lowest  $^2\Pi_g$  state in a linear configuration, formed by a Renner–Teller interaction. The larger spin–orbit interaction present in BeBr<sub>2</sub><sup>+</sup> and BeI<sub>2</sub><sup>+</sup> means these species remain linear. The AIEs and VIEs energies for these species are quite close, which is in line with expectations based on the nonbonding character of the  $\pi_g$  HOMO.

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