

RECEIVED

MAY 14 1999

IN FINAL FORM

JOURNAL OF PHYSICAL CHEMISTRY

Supplementary material

The following tables list the geometries of various  $Al^+(H_2)_n$  and  $AlH_2^+(H_2)_{n-1}$ ,  $n = 2-4$ , stationary points optimized at the MP2/aug-cc-pVTZ level of theory. The results are presented in terms of Cartesian coordinates of all atoms in units of Angstroms.

RECEIVED

AUG 16 1999

REVISED

Table 1. Optimized geometries for  $Al^+(H_2)_2$  and  $AlH_2^+(H_2)$ .

|                              | X         | Y         | Z         |
|------------------------------|-----------|-----------|-----------|
| <i>Electrostatic Complex</i> |           |           |           |
| Al                           | 0.000000  | 0.592017  | 0.000000  |
| H                            | 1.305943  | -2.102533 | 0.000000  |
| H                            | 1.934374  | -1.708029 | 0.000000  |
| H                            | -1.620158 | -1.942831 | 0.370954  |
| H                            | -1.620158 | -1.942831 | -0.370954 |
| <i>Transition State</i>      |           |           |           |
| Al                           | 0.000000  | 0.000000  | 0.359088  |
| H                            | 0.000000  | 1.260205  | -0.719100 |
| H                            | 0.000000  | 0.462845  | -1.614972 |
| H                            | 0.000000  | -1.260205 | -0.719100 |
| H                            | 0.000000  | -0.462845 | -1.614972 |
| <i>Covalent Molecule</i>     |           |           |           |
| Al                           | 0.000000  | 0.000000  | 0.219224  |
| H                            | 0.000000  | 1.528579  | 0.429839  |
| H                            | 0.000000  | -1.528579 | 0.429839  |
| H                            | 0.000000  | 0.378809  | -1.854793 |
| H                            | 0.000000  | -0.378809 | -1.854793 |

SUPPLEMENTARY MATERIAL

Table 2. Optimized geometries for  $\text{Al}^+(\text{H}_2)_3$  and  $\text{AlH}_2^+(\text{H}_2)_2$ 

|                              | X         | Y         | Z         |
|------------------------------|-----------|-----------|-----------|
| <i>Electrostatic Complex</i> |           |           |           |
| Al                           | 0.000000  | 0.000000  | 0.732094  |
| H                            | -0.462770 | 1.598390  | -1.747430 |
| H                            | 0.000000  | 2.080755  | -1.424977 |
| H                            | -1.152862 | -1.199966 | -1.747430 |
| H                            | -1.801987 | -1.040377 | -1.424977 |
| H                            | 1.615632  | -0.398425 | -1.747430 |
| H                            | 1.801987  | -1.040377 | -1.424977 |
| <i>Transition State</i>      |           |           |           |
| Al                           | 0.000000  | 0.439243  | 0.000000  |
| H                            | -0.593531 | -0.418724 | 1.270604  |
| H                            | -0.593531 | -0.418724 | -1.270604 |
| H                            | -0.807002 | -1.272567 | 0.482740  |
| H                            | -0.807002 | -1.272567 | -0.482740 |
| H                            | 1.137665  | -1.437547 | 0.000000  |
| H                            | 1.663402  | -0.890028 | 0.000000  |
| <i>Covalent Molecule</i>     |           |           |           |
| Al                           | 0.000000  | 0.000000  | 0.298655  |
| H                            | 0.000000  | 1.522287  | 0.594547  |
| H                            | 0.000000  | -1.522287 | 0.594547  |
| H                            | -1.387656 | 0.385357  | -1.267903 |
| H                            | 1.387656  | -0.385357 | -1.267903 |
| H                            | 1.387656  | -0.385357 | -1.267903 |
| H                            | 1.387656  | 0.385357  | -1.267903 |

Table 3. Optimized geometry for  $\text{Al}^+(\text{H}_2)_4$ .

|                              | X         | Y         | Z         |
|------------------------------|-----------|-----------|-----------|
| <i>Electrostatic Complex</i> |           |           |           |
| Al                           | 0.000000  | 0.756975  | 0.000000  |
| H                            | 0.248759  | -0.953566 | 2.506142  |
| H                            | -0.287243 | -0.510271 | 2.763577  |
| H                            | -0.287243 | -0.510271 | -2.763577 |
| H                            | 0.248759  | -0.953566 | -2.506142 |
| H                            | 1.919309  | -1.531945 | 0.000000  |
| H                            | 1.289315  | -1.924505 | 0.000000  |
| H                            | -1.565828 | -1.728273 | 0.371192  |
| H                            | -1.565828 | -1.728273 | -0.371192 |

The following tables list the harmonic frequencies ( $\text{cm}^{-1}$ ) at the various  $\text{Al}^+(\text{H}_2)_2$  and  $\text{AlH}_2^+(\text{H}_2)_{n-1}$ ,  $n = 1-3$ , stationary points calculated at the MP2/aug-cc-pVTZ level of theory. Results are presented for per-hydrogenated and per-deuterated species (all with  $^{27}\text{Al}$  isotope) with the group theoretical symmetry of the associated normal mode in parenthesis.

Table 4. Harmonic frequencies for  $\text{Al}^+(\text{H}_2)$  and  $\text{AlH}_2^+$  and their deuterated analogs.

| Electrostatic complex ( $C_{2v}$ ) |                           | Transition State ( $C_s$ ) <sup>a</sup> |                           | Covalent molecule ( $D_{\infty h}$ ) |                           |
|------------------------------------|---------------------------|---|---------------------------|--------------------------------------|---------------------------|
| <i>per-H</i> <sub>2</sub>          | <i>per-D</i> <sub>2</sub> | <i>per-H</i> <sub>2</sub>               | <i>per-D</i> <sub>2</sub> | <i>per-H</i> <sub>2</sub>            | <i>per-D</i> <sub>2</sub> |
| 184.2906 ( $a_1$ )                 | 134.8113 ( $a_1$ )        | 254.5000i ( $a'$ )                      | 181.5638i ( $a'$ )        | 582.0948 ( $\pi_u$ )                 | 425.8109 ( $\pi_u$ )      |
| 366.1424 ( $b_1$ )                 | 259.1455 ( $b_2$ )        | 116.4900 ( $a'$ )                       | 83.9264 ( $a'$ )          | 2084.8597 ( $\sigma_g$ )             | 1474.7849 ( $\sigma_g$ )  |
| 4448.4009 ( $a_1$ )                | 3146.7035 ( $a_1$ )       | 1176.1923 ( $a'$ )                      | 846.4684 ( $a'$ )         | 2173.7895 ( $\sigma_u$ )             | 1590.1588 ( $\sigma_u$ )  |

<sup>a</sup>Calculated at MRCISD/aug-cc-pVTZ level of theory.

Table 5. Harmonic frequencies for  $\text{Al}^+(\text{H}_2)_2$  and  $\text{AlH}_2^+(\text{H}_2)$  and their deuterated analogs.

| Electrostatic complex ( $C_s$ ) |                            | Transition State ( $C_{2v}$ ) <sup>a</sup> |                              | Covalent molecule ( $D_{2v}$ ) |                             |
|---------------------------------|----------------------------|--|------------------------------|--------------------------------|-----------------------------|
| <i>per</i> -H <sub>2</sub>      | <i>per</i> -D <sub>2</sub> | <i>per</i> -H <sub>2</sub>                 | <i>per</i> -D <sub>2</sub>   | <i>per</i> -H <sub>2</sub>     | <i>per</i> -D <sub>2</sub>  |
| 33.4515 (a'')                   | 23.6734 (a'')              | 1811.6170i (a <sub>1</sub> )               | 1306.2005i (a <sub>1</sub> ) | 383.7799 (a <sub>2</sub> )     | 271.4777 (a <sub>2</sub> )  |
| 97.9971 (a')                    | 70.5724 (a')               | 771.5546 (a <sub>1</sub> )                 | 572.5004 (a <sub>1</sub> )   | 470.6658 (b <sub>2</sub> )     | 337.1470 (b <sub>2</sub> )  |
| 114.4904 (a'')                  | 80.9881 (a'')              | 853.9640 (b <sub>1</sub> )                 | 603.7980 (b <sub>1</sub> )   | 513.7408 (a <sub>1</sub> )     | 383.5984 (a <sub>1</sub> )  |
| 184.7688 (a')                   | 134.0588 (a')              | 1220.3350 (a <sub>2</sub> )                | 879.5862 (a <sub>2</sub> )   | 586.1778 (b <sub>1</sub> )     | 431.3569 (b <sub>1</sub> )  |
| 188.7808 (a')                   | 138.6870 (a')              | 1247.8160 (b <sub>2</sub> )                | 888.4574 (b <sub>2</sub> )   | 671.2849 (a <sub>1</sub> )     | 477.8314 (a <sub>1</sub> )  |
| 363.3553 (a'')                  | 257.1752 (a'')             | 1328.6289 (b <sub>2</sub> )                | 963.1555 (b <sub>2</sub> )   | 895.9154 (b <sub>2</sub> )     | 634.9747 (b <sub>2</sub> )  |
| 375.2626 (a')                   | 265.6690 (a')              | 1699.3047 (a <sub>1</sub> )                | 1235.5384 (a <sub>1</sub> )  | 2096.3038 (a <sub>1</sub> )    | 1483.9016 (a <sub>1</sub> ) |
| 4445.5498 (a')                  | 3144.6870 (a')             | 1738.7847 (b <sub>2</sub> )                | 1271.0283 (b <sub>2</sub> )  | 2174.0993 (b <sub>2</sub> )    | 1589.8361 (b <sub>2</sub> ) |
| 4447.0869 (a')                  | 3145.7740 (a')             | 2236.2229 (a <sub>1</sub> )                | 1544.8718 (a <sub>1</sub> )  | 4230.6004 (a <sub>1</sub> )    | 2992.6547 (a <sub>1</sub> ) |

Table 5. Harmonic frequencies for  $Al^+(H_2)_3$  and  $AlH_2^+(H_2)_2$  and their deuterated analogs.

| Electrostatic complex ( $C_3$ ) |                            | Transition State ( $C_s$ ) <sup>a</sup> |                            | Covalent molecule ( $C_{2v}$ ) |                             |
|---------------------------------|----------------------------|---|----------------------------|--------------------------------|-----------------------------|
| <i>per</i> -H <sub>2</sub>      | <i>per</i> -D <sub>2</sub> | <i>per</i> -H <sub>2</sub>              | <i>per</i> -D <sub>2</sub> | <i>per</i> -H <sub>2</sub>     | <i>per</i> -D <sub>2</sub>  |
| 86.3143 (e)                     | 61.2664 (e)                | 1823.8316i (a')                         | 1296.1763i (a')            | 281.1815 (a <sub>1</sub> )     | 203.3514 (a <sub>1</sub> )  |
| 86.3143 (e)                     | 61.2664 (e)                | 184.1765 (a'')                          | 130.4489 (a'')             | 335.4768 (a <sub>2</sub> )     | 237.3091 (a <sub>2</sub> )  |
| 105.9722 (e)                    | 75.1320 (e)                | 378.8169 (a')                           | 281.0468 (a')              | 373.5730 (b <sub>2</sub> )     | 264.3102 (b <sub>2</sub> )  |
| 105.9722 (e)                    | 75.1320 (e)                | 465.8735 (a')                           | 335.2461 (a')              | 465.9618 (b <sub>2</sub> )     | 330.8865 (a <sub>2</sub> )  |
| 115.0184 (a)                    | 83.9980 (a)                | 607.8916 (a'')                          | 431.9841 (a'')             | 467.7644 (a <sub>2</sub> )     | 337.2227 (b <sub>2</sub> )  |
| 168.3656 (a)                    | 119.1033 (a)               | 797.9041 (a')                           | 574.7195 (a')              | 527.2719 (a <sub>1</sub> )     | 392.8800 (a <sub>1</sub> )  |
| 188.3378 (a)                    | 137.9037 (e)               | 834.8376 (a')                           | 606.5273 (a')              | 528.760 (b <sub>1</sub> )      | 395.2613 (b <sub>1</sub> )  |
| 191.2002 (e)                    | 137.9037 (e)               | 925.2437 (a')                           | 654.6304 (a')              | 654.2074 (b <sub>1</sub> )     | 466.5552 (b <sub>1</sub> )  |
| 191.2002 (e)                    | 140.1917 (a)               | 1141.2062 (a'')                         | 807.9733 (a'')             | 677.2638 (a <sub>1</sub> )     | 483.1822 (a <sub>1</sub> )  |
| 373.4858 (e)                    | 264.4050 (e)               | 1310.9170 (a'')                         | 928.0565 (a'')             | 912.2339 (a <sub>2</sub> )     | 645.2947 (a <sub>2</sub> )  |
| 373.4858 (e)                    | 264.4050 (e)               | 1443.9333 (a'')                         | 1030.8927 (a'')            | 921.8320 (b <sub>2</sub> )     | 654.7998 (b <sub>2</sub> )  |
| 377.0349 (a)                    | 266.9857 (a)               | 1776.3995 (a')                          | 1265.0829 (a')             | 2099.3935 (a <sub>1</sub> )    | 1487.0145 (a <sub>1</sub> ) |
| 4442.2403 (a)                   | 3142.3464 (a)              | 1840.3461 (a'')                         | 1318.2373 (a'')            | 2166.4203 (b <sub>1</sub> )    | 1583.4283 (b <sub>2</sub> ) |
| 4443.8334 (e)                   | 3143.4725 (e)              | 1997.2521 (a')                          | 1413.3284 (a')             | 4230.2965 (b <sub>1</sub> )    | 2992.4362 (b <sub>1</sub> ) |
| 4443.8334 (e)                   | 3143.4725 (e)              | 4174.6538 (a')                          | 2953.0928 (a')             | 4235.7444 (a <sub>1</sub> )    | 2996.2979 (a <sub>1</sub> ) |

Table 6. Harmonic frequencies for  $Al^+(H_2)_4$  and the deuterated analog.

| Electrostatic complex ( $C_3$ ) |                                 |
|---------------------------------|---------------------------------|
| <u><i>per-H<sub>2</sub></i></u> | <u><i>per-D<sub>2</sub></i></u> |
| 65.4466 (a')                    | 47.1509 (a')                    |
| 80.2030 (a'')                   | 56.7446 (a'')                   |
| 81.1239 (a')                    | 58.5157 (a')                    |
| 109.4968 (a'')                  | 77.7117 (a'')                   |
| 113.1515 (a'')                  | 80.5928 (a'')                   |
| 115.3197 (a')                   | 82.8172 (a')                    |
| 121.1706 (a')                   | 87.0234 (a')                    |
| 135.3876 (a'')                  | 96.4936 (a'')                   |
| 173.8592 (a'')                  | 128.0864 (a'')                  |
| 186.3565 (a')                   | 132.7261 (a')                   |
| 189.3319 (a'')                  | 133.9956 (a'')                  |
| 189.9841 (a')                   | 138.8940 (a')                   |
| 194.8260 (a')                   | 142.1348 (a')                   |
| 357.6015 (a')                   | 253.0159 (a'')                  |
| 357.6503 (a'')                  | 253.3875 (a')                   |
| 376.0542 (a')                   | 266.3009 (a')                   |
| 384.7123 (a'')                  | 272.3869 (a'')                  |
| 4439.8327 (a')                  | 3140.6432 (a')                  |
| 4441.8128 (a')                  | 3142.0433 (a')                  |
| 4450.0495 (a'')                 | 3147.8702 (a'')                 |
| <u>4451.7845 (a')</u>           | <u>3149.0968 (a')</u>           |