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The lowest ionization potentials of Al_2

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Abstract

Potential curves for the lowest two electronic states ($X^2\Sigma_g^+$ and $A^2\Pi_u$) of Al_2^+ have been computed using complete active space SCF/multireference CI wave functions and large Gaussian basis sets. The lowest observable vertical ionization potential (to Al_2^+ $X^2\Sigma_g^+$) of the Al_2 $X^3\Pi_u$ ground state is calculated to occur around 6.1 eV, in excellent agreement with the experimental range of 6.0–6.42 eV obtained in recent cluster ionization studies by Cox and co-workers. The second vertical ionization potential (to Al_2^+ $A^2\Pi_u$) occurs near 6.4 eV, also within the experimental range. The adiabatic IP of 5.90 eV is in good agreement with the value of 5.8-6.1 eV deduced by Hanley and co-workers from the difference in thresholds between collision induced dissociation processes of Al_3^+. The computed IP values are somewhat larger than those deduced from branching ratios in cluster fragmentation experiments by Jarrold and co-workers. The observation of an ionization threshold below 6.42 eV is shown to be incompatible with an Al_2 ground electronic state assignment of $^3\Sigma_g^-$, but the separation between the two lowest states of Al_2 is so small that it is likely that both are populated in the experiments, so that this does not provide unambiguous support for the recent theoretical assignment of the ground state as $^3\Pi_u$.

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I. Introduction

Recent studies of aluminum clusters by Jarrold *et al.* [1], Hanley *et al.* [2], and Cox *et al.* [3] have provided estimates of cluster ionization potentials. While these sources agree for most ionization potentials of Al_n, $n < 15$, Jarrold *et al.* inferred a value for Al_2 of 5.5 eV, outside the range of 6.0–6.4 eV obtained by Cox *et al.* Hanley *et al.* deduced a value of 5.8 eV, but noted that the dissociation might involve a spin-forbidden process; correcting for this gave a value of 6.2 eV. (This should be revised to 6.1 eV using the splitting between the lowest singlet and triplet states of Al_2 ($a^1\Sigma_g^+$–$X^3\Pi_u$) from the best available calculation [4]). The work of Cox *et al.* involves laser photoionization of a cluster beam followed by mass spectrometric analysis of the resulting cluster ions, and it would be expected that the failure to observe production of Al_2^+ with laser energies below 6 eV provides a reliable lower bound for the ionization potential of Al_2. The result of Jarrold *et al.* is obtained from analysis of the branching ratios in observations of fragmentation of Al_3^+ cluster ions, and is therefore a less direct measurement than that of Cox *et al.* Using the data analysis method of Jarrold *et al.*, Hanley *et al.* obtained a value of 5.2 eV. Upton [5] has calculated a vertical IP for the $X^3\Pi_u$ state of Al_2 of 6.02 eV. However, the same level of theory incorrectly predicts the ground state of Al_2 to be $^3\Sigma_g^-$, lying 0.06 eV below the $^3\Pi_u$ state [6]. Sunil and Jordan [7] have computed vertical and adiabatic IPs of 6.12 and 5.92 eV using the coupled-cluster double excitation approach including single and triple excitations (CCD+ST(CCD)). This approach was in reasonable agreement with the best calculations for the Al_2 $X^3\Pi_u$–$A^3\Sigma_g^-$ separation [4] and the calculated IP is in good agreement with the work of Cox *et al.* However, since the available experimental values for the Al_2 IP vary so markedly, it is worthwhile reconsidering this problem with a higher level of theory than has been used previously.

In a recent study of the low-lying states of Al_2, Bauschlicher *et al.* [4] concluded that the ground state was $^3\Pi_u$, but that the first excited state, $^3\Sigma_g^-$, was only 180 cm^{-1} higher in energy, with the $^1\Sigma_g^+$ state lying some 2 000 cm^{-1} above the ground state. While the separation between the lowest two states is very small, the reliability of the prediction was established by performing full CI benchmark calculations to calibrate the appropriate computational method (a complete active space SCF (CASSCF) calculation followed by a multireference CI calculation with all CASSCF configurations used as reference configurations — second-order CI (SOCI)); this method was then applied in a very large atomic basis set, so that errors due to basis set incompleteness or an inadequate treatment of correlation were essentially eliminated. As this SOCI approach has been shown to be very reliable in the calculation of ionization potentials (IPs) of other systems with the same number of valence electrons as Al_2 [8], this approach offers a way of accurately computing the IPs of Al_2, and thereby characterizing the low-lying states of Al_2^+ and possibly rationalizing the discrepancies between the existing experiments.

In the next section we describe briefly the computational methods (a more complete discussion is given in Ref. 4), in section III we discuss the computed results, and our conclusions are given in section IV.

II. Methods

The contracted Gaussian basis used is the [6*s* 5*p* 3*d* 2*f*] set from Ref. 4, which is a general contraction, based on atomic natural orbitals, of a (20*s* 13*p* 6*d* 4*f*) primitive basis. All results presented in this work were obtained using CASSCF/SOCI wave functions. The active space for the CASSCF calculations comprised those molecular orbitals derived from the atomic 3*s* and 3*p* orbitals, with six active electrons for the neutral and five for the ionic states. Only these electrons were correlated in the SOCI calculations. This procedure is known to produce excellent spectroscopic constants for Al_2, where it has been calibrated against full CI calculations, and it can be expected to perform equally well for Al_2^+. In this regard, we note that for r(Al-Al)=100 a_0, the IP is 5.93 eV, or 0.05 eV smaller than the experimental value for Al atom [9]. Thus we expect our computed IPs of Al_2 to be systematically about 0.05-0.10 eV too small.

Spectroscopic constants (r_e, ω_e) were obtained from a fit in $1/r$ to three points around the minimum of each curve. D_e values were obtained using a supermolecule approach at r=100 a_0 to reduce size-consistency errors. For the calculation of Franck-Condon factors, the potential curves were represented by a tensioned cubic spline interpolation of the computed energy points, and vibrational wave functions were obtained by numerical integration.

All calculations were performed using the MOLECULE-SWEDEN [10,11] codes on the NAS Facility CRAY 2.

III. Results and discussion

Potential curves for the $X^3\Pi_u$ and $A^3\Sigma_g^-$ states of Al_2 and the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of Al_2^+ are displayed in Fig. 1, and the corresponding spectroscopic constants are listed in Table I. The Al_2 $X^3\Pi_u$ ground state wavefunction is dominated by the open-shell configuration $\sigma_g^1\pi_u^1$, while the $A^3\Sigma_g^-$ excited state wavefunction is dominated by the open-shell configuration π_u^2. Since a shorter bond distance is required for effective π bonding, the bond length of the $X^3\Pi_u$ state would be expected to be longer, as observed, and the same effect manifests itself in the Al_2^+ states: the $X^2\Sigma_g^+$ ground state has a σ_g bonding electron and a considerably longer bond than the $A^2\Pi_u$ state with its single π_u bonding electron. Although the bond lengths in all the neutral and ionic states listed in Table I are rather large, all the states have significant ($\approx$ 1 eV or more) binding energies. It is interesting to note that for Al_2, the difference in energy between the $A^3\Sigma_g^-$ and the $X^3\Pi_u$ states is very small (0.02 eV), whereas the difference in energy for the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of Al_2^+ is much larger (0.52 eV). This is despite the fact that the occupations of the Al_2 and Al_2^+ states differ only in the single π_u electron. The reason for the large difference comes from the increased electrostatic contribution to the bonding in Al_2^+. The σ_g electron in the $^2\Sigma_g^+$ state shields the positively charged Al centers from each other, thus reducing the electrostatic repulsion this effect is not present for the $^2\Pi_u$ state. In addition, the much shorter bond length of the $^2\Pi_u$ state leads to a greatly increased electrostatic repulsion compared to the $^2\Sigma_g^+$ state. Thus the $^2\Sigma_g^+$ state is significantly more stable than the $^2\Pi_u$ state for Al_2^+. Finally, we note that the spectroscopic constants of Table I are in good agreement with those obtained by Sunil and Jordan [7] using a smaller basis set and the CCD+ST(CCD) method.

It is clear from the potential curves of Fig. 1 that the $X^3\Pi_u \rightarrow A^2\Pi_u$ ionization will have very similar values for the adiabatic and vertical IPs, whereas the large difference in r_e for the ground and ionized states for the $X^3\Pi_u \rightarrow X^2\Sigma_g^+$ and $A^3\Sigma_g^- \rightarrow A^2\Pi_u$ ionizations leads to a considerable difference between their adiabatic and vertical IPs. The IP values listed in Table II confirm these qualitative deductions.

We note that since the $A^3\Sigma_g^-$ state cannot ionize to the $X^2\Sigma_g^+$ state by a one-electron process, the intensity for this ionization is expected to be very low. Like the spectroscopic constants, the IPs are in good agreement with the results of Sunil and Jordan [7]. The vertical values correspond to that ionization from the $v'' = 0$ level of the appropriate neutral dimer state that has the largest Franck-Condon factor, as given in Table III. Only ionizations from $v'' = 0$ levels are listed: other values may be calculated from the potential curves, the computed energies defining which are listed in the Appendix. The most probable transitions for the lowest ionization process, $X^3\Pi_u \rightarrow X^2\Sigma_g^+$, are actually to the levels around $v' = 12$ at 49 537 cm^{-1}, some 2000 cm^{-1} above the adiabatic value. The next lowest energy ionization process is $X^3\Pi_u \rightarrow A^2\Pi_u$, which has a vertical IP of around 51 851 cm^{-1}, the same as the adiabatic value. Finally, ionization from the $A^3\Sigma_g^-$ excited state will occur mainly to the levels $v' = 2$ and somewhat higher, beginning at 52 080 cm^{-1}.

These results are completely consistent with the experimental observations of Cox *et al.* [3] We predict that there will be little or no intensity from ionization into the lowest levels of Al_2^+ $X^2\Sigma_g^+$, so that although the lowest adiabatic IP for Al_2 is below 6 eV (and is, in fact, some 600 cm^{-1} less than that of Al atom), the experimental threshold for observing ionization of Al_2 will indeed be between 6.0 and 6.42 eV, as noted by Cox *et al.* At photoionization energies above 6.42 eV, ionization from the Al_2 $X^3\Pi_u$ state to give the $A^2\Pi_u$ state of the ion will also be observed. Further, if (as seems very likely under the experimental conditions of Ref. 3) the $A^3\Sigma_g^-$ state of Al_2 is significantly populated, ionization from this state to the $A^2\Pi_u$ ion state will also occur at photon energies above 6.42 eV.

In addition to providing a complete explanation of the ionization threshold behavior observed by Cox *et al.* [3], the above results suggest another method for confirming the assertion in Ref. 4 that the ground state of Al_2 is indeed $^3\Pi_u$. While the full CI calibration calculations described in Ref. 4 should provide a very small error bar for the prediction of a $^3\Pi_u$ ground-state, it must be admitted that the estimated separation between the two lowest triplet states is very small. However, the $^3\Sigma_g^-$ state can only ionize to give $^2\Pi_u$, a process with a computed energy threshold of almost 6.5 eV, some 0.4 eV above the onset of ionization from $^3\Pi_u$. The error associated with this theoretical prediction can hardly be greater than a few hundredths of an eV. Therefore, if Al_2 molecules could be generated in a source that allowed almost complete cooling of the electronic degrees of freedom, the observation of an ionization threshold of around 6 eV would provide absolute confirmation of a $^3\Pi_u$ ground state for Al_2. However, we note that the presence of Al atoms, which also ionize above this threshold, may complicate performing such an experiment.

While the current results agree well with the experimental results of Cox *et al.* [3], they differ considerably from those of Jarrold *et al.* [1] These workers infer an (essentially adiabatic) ionization potential of around 5.5 eV for Al_2, considerably smaller than our estimate. However, the analysis of cluster ion fragmentation used to obtain this estimate in Ref. 1 may not be reliable for Al_3^+, which is the species used to estimate the Al_2 IP. As noted previously, Hanley *et al.* [2] obtain a value of only 5.2 eV using the analysis of Jarrold *et al.*, compared with 5.8 eV from their own analysis. While cluster ions Al_n^+ with $n \leq 11$ primarily fragment to Al_{n-1} and Al^+, Al_3^+ fragments to give mainly Al_2^+ and Al. This in turn suggests that a number of the hypotheses used in inferring the ionization potentials, such as the similarity between transition states on various dissociation pathways, may not be valid. It should be noted that Jarrold *et al.* also point to the fact that dissociation of Al_3^+ to give Al_2 and Al^+ is spin-forbidden as a possible source of error in their analysis (or at least in comparison of their work with that of other groups). However, as noted above, this is not observed to be the primary fragmentation pathway for Al_3^+, and the observed fragmentation to give Al_2^+ and Al is spin-allowed independent of whether the ground state of Al_3^+ is a triplet or a singlet. It seems improbable that this is the basis for the disagreement between the results of Jarrold *et al.* with those of Cox *et al.* and the present work: it seems more likely that the model of cluster ion fragmentation used in Ref. 1 is simply not valid for the smallest cluster ions.

The result of Hanley *et al.* [2] (5.8 eV) is expected to correspond to the adiabatic IP. As they noted, the $Al_3^+ \rightarrow Al_2 + Al^+$ path is expected to be spin forbidden and therefore their IP should be corrected by the splitting between the lowest singlet and triplet states for Al_2. They used the $^1\Sigma_g^+$–$^3\Sigma_g^-$ separation of 0.4 eV from the work of Upton [6], which incorrectly predicts a $^3\Sigma_g^-$ ground state for Al_2. However, better calculations [4] yield a value of 0.3 eV for the singlet–triplet correction, based on the $^1\Sigma_g^+$–$^3\Pi_u$ separation; this would result in an IP of 6.1 eV. This is in reasonable agreement with our computed value of 5.90 eV (≈5.95-6.00 eV if we correct our IP for the error in the computed Al atom IP). Thus it appears that the method of Hanley *et al.* obtains reasonable estimates for the cluster IPs. It should be noted that their method should become more reliable as the clusters increase in size, as the difference in energy between states of different spin will be even smaller.

Our computed Al_2 adiabatic IP of 5.90 eV is slightly less than the Al atom IP of 5.93 eV [9], using the same level of treatment. Thus the Al_2 IP is smaller than the Al IP, as suggested by Jarrold *et al.* [1], although only by a very small amount. Upton [5] has computed a vertical IP for Al_2 of 6.02 eV for the $^3\Pi_u$ state, in a smaller basis set and at a lower level of correlation treatment than in the present work. As we noted above this level of treatment incorrectly predicts a $^3\Sigma_g^-$ ground state for Al_2, thus the modest difference with the present work is not unexpected. The results of Sunil and Jordan [7] are in good agreement with the present calculations, and therefore we conclude that the CCD+ST(CCD) level of treatment gives a good description of this system.

IV. Conclusions.

Large-scale multireference CI calculations in an extended basis set predict the lowest adiabatic IP of Al_2 to be 5.90 eV, very close to that of Al atom. However, the lowest vertical IP is predicted to be at least 0.25 eV larger than the adiabatic value because of the large increase in r_e on ionization. This is consistent with the observation of Cox *et al.* [3] that the threshold for ionization is between 6.0 and 6.42 eV, and suggests that the inferred adiabatic IP of 5.5 eV of Jarrold *et al.* [1] is much too low. The IP of Hanley *et al.* [2], if corrected with the best estimate of the singlet–triplet separation in Al_2, is also in good agreement with the computed values. At ionization energies above 6.4 eV, ionization to give the excited Al_2^+ $A^2\Pi_u$ state can occur, as can ionization from the $A^3\Sigma_g^-$ state of Al_2 if the experimental conditions are such that this state is appreciably populated. It is suggested that the observation of ionization below 6.42 eV in electronically cold Al_2 would confirm the assertion that the ground state of Al_2 is indeed $^3\Pi_u$.

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Table I. Al_2^a and Al_2^+ spectroscopic constants.

	r_e (Å)	ω_e (cm^{-1})	D_e (eV)	T_e (cm^{-1})
$X^3\Pi_u$	2.727	278	1.40	
$A^3\Sigma_g^-$	2.492	345	1.38	165
$X^2\Sigma_g^+$	3.212	169	1.42	
$A^2\Pi_u$	2.794	218	0.90	4214

[a] From Ref. 4.

Table II. Adiabatic and vertical ionization potentials (eV) of Al_2.

	Adiabatic	Vertical
$X^3\Pi_u \rightarrow X^2\Sigma_g^+$	5.90	6.14
$A^3\Sigma_g^- \rightarrow A^2\Pi_u$	6.40	6.53
$X^3\Pi_u \rightarrow A^2\Pi_u$	6.43	6.43

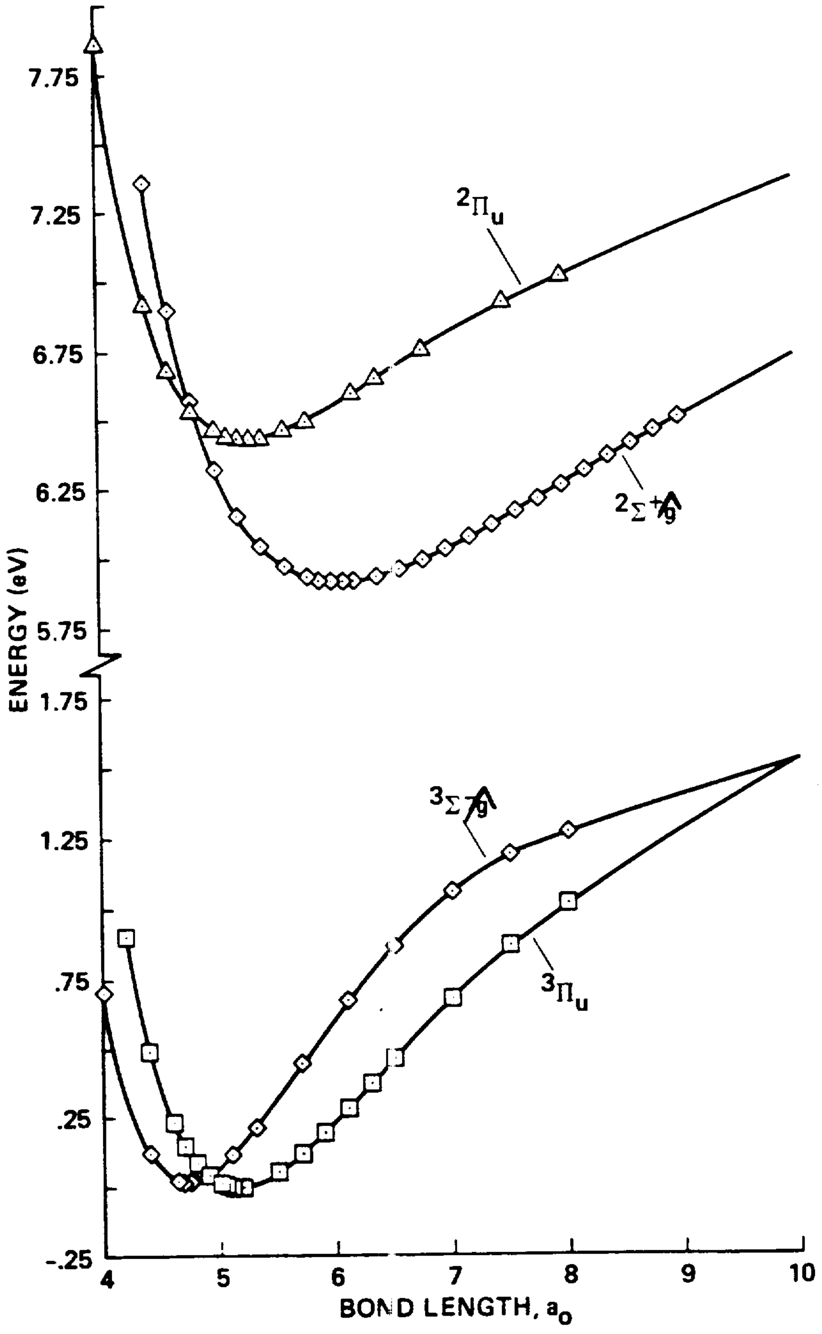
Table III. Franck-Condon factors ($q_{v'0}$) for ionization of Al_2 from $v''=0$.

	$X^3\Pi_u \rightarrow X^2\Sigma_g^+$		$A^3\Sigma_g^- \rightarrow A^2\Pi_u$		$X^3\Pi_u \rightarrow A^2\Pi_u$	
v'	$q_{v'0}$	$\Delta E(\mathrm{cm}^{-1})$	$q_{v'0}$	$\Delta E(\mathrm{cm}^{-1})$	$q_{v'0}$	$\Delta E(\mathrm{cm}^{-1})$
0	0.0000	47 612	0.7855	51 851	0.0065	51 651
1	0.0003	47 781	0.1933	52 067	0.0268	51 868
2	0.0012	47 948	0.0204	52 281	0.0591	52 081
3	0.0036	48 114	0.0009	52 490	0.0937	52 290
4	0.0081	48 278			0.1196	52 496
5	0.0152	48 441			0.1305	52 698
6	0.0250	48 602			0.1264	52 897
7	0.0367	48 761			0.1114	53 092
8	0.0491	48 919			0.0912	53 283
9	0.0608	49 076			0.0704	53 472
10	0.0703	49 231			0.0519	53 657
11	0.0769	49 385			0.0370	53 838
12	0.0799	49 537			0.0256	54 017
13	0.0795	49 688			0.0173	54 192
14	0.0761	49 837			0.0115	54 364
15	0.0704	49 985			0.0076	54 532
16	0.0632	50 132			0.0049	54 697
17	0.0552	50 277			0.0032	54 859
18	0.0470	50 421			0.0020	55 018
19	0.0392	50 564			0.0013	55 173
20	0.0321	50 705			0.0008	55 325
21	0.0258	50 845			0.0005	55 473
22	0.0204	50 984			0.0003	55 618
23	0.0159	51 122			0.0002	55 759
24	0.0123	51 258			0.0001	55 897

Appendix. The total SOCI energies in E_H, relative to -483.0.

	Al_2^+		Al_2	
	$A^2\Pi_u$	$X^2\Sigma_g^+$	$X^3\Pi_u$	$A^3\Sigma_g^-$
3.50	−0.527 204		−0.813 463	
4.00	−0.628 335		−0.891 857	
4.20			−0.884 491	
4.40	−0.662 954	−0.646 938	−0.899 496	−0.913 176
4.60	−0.671 830	−0.664 080	−0.908 993	
4.65				−0.916 649
4.70			−0.912 152	−0.916 759
4.75				−0.916 714
4.80	−0.677 145	−0.676 493	−0.914 458	−0.916 530
4.90			−0.916 038	−0.915 800
5.00	−0.679 961	−0.685 345	−0.917 005	
5.10	−0.680 682		−0.917 455	−0.913 213
5.15			−0.917 512	
5.20	−0.681 049	−0.691 514	−0.917 469	
5.30	−0.681 125			−0.909 629
5.40	−0.680 962	−0.695 658		
5.50			−0.915 566	
5.60	−0.680 094	−0.698 269		
5.70			−0.913 192	−0.901 165
5.80	−0.678 720	−0.699 721		
5.90		−0.700 103	−0.910 294	
6.00		−0.700 297		
6.10		−0.700 326	−0.907 091	−0.892 719
6.20	−0.675 181	−0.700 213		
6.30			−0.903 749	
6.40	−0.673 248	−0.699 633		
6.50			−0.900 386	−0.885 410
6.60		−0.698 684		
6.80	−0.669 398	−0.697 462		
7.00		−0.696 040	−0.892 405	−0.878 458
7.20		−0.694 474		
7.40		−0.692 810		
7.50	−0.663 371		−0.885 566	−0.873 790
7.80		−0.691 080		
7.90		−0.689 312		
8.00	−0.659 859	−0.687 527	−0.880 113	−0.870 842
8.20		−0.685 741		
8.40		−0.683 967		
8.60		−0.682 217		
8.80		−0.680 497		
9.00		−0.678 816		
100.	−0.648 109	−0.648 204	-0.866 026	

Figure Caption.
The Al_2 and Al_2^+ potential energy curves, relative to the Al_2 $X^3\Pi_u$ ground state minimum.



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