

Spectroscopic studies of the jet-cooled aluminum trimer

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Gas phase spectroscopic investigations of the jet-cooled aluminum trimer are reported using the technique of resonant two-photon ionization with mass spectrometric detection. A discrete band system in the 5200–6100 Å region is observed, consisting of an extended vibrational progression in a single vibrational mode. In addition, an apparent continuum absorption is observed which gradually grows in toward shorter wavelengths. The apparent continuum exhibits a long lifetime, 24–35 μs, which is most unusual and indicates that the continuum arises from spectral congestion and not lifetime broadening. At 19 378 cm⁻¹ both the discrete and the continuum absorptions terminate abruptly, indicating the onset of dissociation above this energy. Although it is not certain that dissociation above this energy leads to ground electronic state Al₂, this measurement nevertheless places an upper limit on $D_0(\text{Al}_2-\text{Al})$ of 2.40 eV.

I. INTRODUCTION

The electronic structure of metals, and its development as one proceeds from the isolated metal atom to the bulk solid metal, is a topic of considerable current interest in many branches of chemistry and physics. As with all molecules and solids, it is the electronic structure which ultimately determines the structural, physical, and chemical properties of metals and metal clusters. For the metal clusters, these properties are of particular importance to the fields of heterogeneous catalysis, surface chemistry, and solid-state physics, and it is the relevance of metal clusters to these diverse disciplines that has been largely responsible for the recent burst of research activity on these systems.

In theoretical chemistry a major unresolved problem, which is a focus of current research,¹⁻⁵ is the development of a unified description of metal electronic structure, over the entire size range from atoms and small clusters up to the bulk infinite solid. The development of such a unified theory is no simple task, since it is difficult enough to treat the small metal clusters accurately without attempting to correctly extrapolate to the bulk metal. The fundamental difficulty which hampers theoretical efforts in this regard is an inescapable characteristic of metallic systems: metals possess a very high density of low-lying electronic states, and this density of states increases geometrically with increasing cluster size. The presence of such a high density of electronic states at low energies renders the concept of a single-configuration electronic wave function useless, and enables the electronic motion in a metal or metal cluster to be highly correlated. The necessity of a correct theoretical description of such highly correlated electronic states contributes much to the theoretical difficulties in this field. In addition, however, low-lying electronic states of many different spin multiplicities are typically present, so exchange effects must be calculated to high accuracy for an acceptable theoretical de-

scription of a typical small metal cluster. Coupled with these problems are the many different possible geometries of a given small metal cluster. This additional complexity forces the theoretician to repeat his Herculean efforts to accurately describe the important exchange and correlation effects at many different geometries. Of course, the number of possible geometries increases dramatically with cluster size as well. Finally, it is not atypical for the dominant atomic configuration in a metal cluster to change rather dramatically with cluster size, and the basis sets used in calculations must be flexible enough to accurately describe all of the potentially important atomic configurations. Thus, for example, the alkaline earth metals change from a dominant atomic configuration of ns^2 in the smallest clusters (which have only weak van der Waals interactions between atoms), to atomic configurations with a sizable $nsnp$ contribution at larger cluster sizes and in the bulk metal.⁶⁻⁸ Similarly, aluminum may change from a dominant configuration of $3s^23p$ in the smallest clusters to a more strongly bonding dominant configuration of $3s3p^2$ in the larger clusters. With all of these problems to be overcome in the theoretical treatment of metal clusters, it will be extremely important to have detailed experimental data which may be used to test the various theoretical methods, and to contribute to our direct understanding of metal clusters.

Considerable experimental effort is now being directed toward the investigation of metal clusters as functions of cluster size. Rapid progress is being made in the measurement of ionization potentials⁹⁻¹³ and electron affinities¹⁴ of uncharged metal clusters, and the chemical reactivity of both neutral¹⁵⁻²¹ and ionized²²⁻²⁶ metal cluster species with various reactants is under active investigation. The fragmentation patterns²⁷⁻²⁹ and dissociation thresholds²⁹⁻³¹ of mass-selected metal cluster ions have also been measured for some systems. Historically, however, our most direct experimental knowledge of molecular electronic and geometrical structure has been obtained through various spectroscopic methods, and it is likely that spectroscopic investigations will

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provide the greatest insight into the electronic structure of metal clusters as well.

A fundamental problem in spectroscopic investigations of metal clusters is that of the unambiguous identification of the carrier of a spectroscopic transition. In matrix isolation studies this is a severe problem, because it is impossible to couple the spectroscopic investigation to a mass spectrometrically based detection scheme. In favorable cases (especially in ESR³² or Raman spectroscopy³³) isotopic information may permit definite assignments of the carrier of a transition, but one must be very careful even then.^{34,35} Gas-phase studies based on resonant two-photon ionization spectroscopy followed by mass spectrometric detection³⁶ offer one way of uniquely identifying the carrier of a spectroscopic transition. A second gas-phase method which provides unambiguous assignments of the carrier of a transition is the recently developed method of photoelectron spectroscopy of mass-selected metal cluster anions,^{37,38} which shows great promise for revealing the electronic structure of metal clusters.

Apart from the recent results using photoelectron spectroscopy of mass-selected metal cluster anions, no gas-phase spectroscopic results are currently available for metal clusters larger than triatomic. Published gas-phase spectra of triatomic metals are very rare as well, with Na_3 ^{39–41} and Cu_3 ^{42–44} as the only well-analyzed examples. Chemical bonding in both of these species is completely dominated by the *s* electrons, and in both systems the ground state is derived from an electronic configuration of $(a_1')^2e', ^2E'$, (in D_{3h} symmetry), which is subject to a Jahn–Teller distortion. In this paper we present the first gas-phase optical spectrum to be obtained for a metal trimer bound by *p* electrons, Al_3 . In this system there are many more possibilities for chemical bonding than can occur in the *s*-bonded trimers. It is possible in principle, for example, to form π bonds in which the molecular plane is also a nodal plane of a π orbital. Alternatively, Al_3 may be held together primarily by σ bonds derived from the atomic $3p$ orbitals. Finally, there is the (unlikely) possibility of promoting an aluminum atom to the $3s3p^2$ atomic configuration, thereby opening the $3s$ subshell and allowing two more electrons to actively engage in chemical bonding. With all of these possibilities operating in the same chemical species one would expect many low-lying electronic states in Al_3 , as has been confirmed in recent calculations.^{2,45,46}

In Sec. II we present a brief description of our experimental apparatus and methods, and in Sec. III our results for aluminum trimer are presented. In Sec. IV the spectroscopic data are interpreted, and Sec. V concludes this paper with a summary of our results.

II. EXPERIMENTAL

The metal cluster source and molecular beam apparatus used in the present study is quite similar to that used in previous investigations,^{36,42} so only a cursory description is presented here. A scale drawing of the apparatus is given in Fig. 1, omitting details of the cluster source which are provided elsewhere.^{36,47} A pulsed supersonic beam of aluminum clusters is produced by laser vaporization of an aluminum rod³⁶ (Alfa, 1/4 in. diameter, 99.9995% pure) or an aluminum

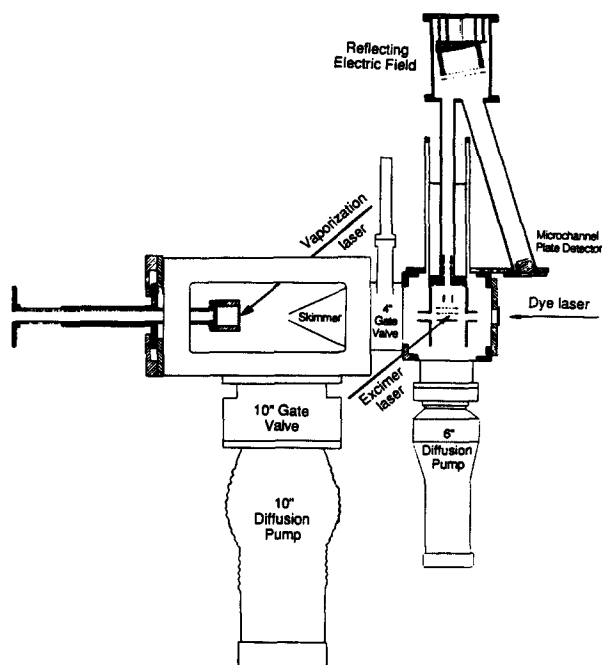


FIG. 1. Scale drawing of the jet-cooled cluster beam spectrometer used in this work. Metal clusters are produced in the large vacuum chamber at the left by laser vaporization, expand into vacuum, pass through a large skimmer, and enter the ionization region of the reflectron TOFMS. Following ionization, the ions are accelerated up the vertical flight tube and reflected down the angled flight tube to the detector.

disk⁴⁷ (stock aluminum, 6061 alloy) located within the throat of a pulsed supersonic nozzle using the second harmonic output (532 nm, 40–80 mJ/pulse) of a *Q*-switched Nd:YAG laser (Quantel, model 580-10). The laser is focused by a 100 cm focal length lens to a 0.5 mm diameter spot on the target rod or disk, and is synchronized to fire coincidentally with the peak density of helium carrier gas, which is pulsed over the target by a magnetically operated double solenoid valve.³⁶ Helium, purified by flowing through a molecular sieve trap maintained at 77 K, is regulated to a pressure of 160 psi for use as the carrier gas. The high density of helium in the 2 mm diameter nozzle throat then serves to quench the plasma produced by laser vaporization, and provides sufficient three-body collisions for cluster formation to occur.

The helium carrier gas, along with the aluminum clusters entrained within it, then expands freely into a vacuum chamber maintained at 7×10^{-4} Torr, and the internal degrees of freedom of the clusters are cooled in the resulting supersonic expansion. The free jet is then collimated by a conical skimmer (Beam Dynamics, 5 mm diameter, 50° inside angle) after which it enters a second chamber maintained at 2×10^{-5} Torr. Within this chamber the beam enters the ionization region of a homemade reflectron-type^{48–53} time-of-flight mass spectrometer. Ionization of the clusters is achieved by either direct one-photon or resonant two-photon ionization, following which the ions are accelerated up a vertical flight tube approximately 0.9 m in length. At the apex of this flight tube is mounted a reflecting electric field assembly, which reflects the ions down a second flight tube mounted at an angle of 18° with respect to the first flight

tube. Ion detection is accomplished with a microchannel plate detector (Galileo, model 3025-B) coupled to a 50 Ω anode assembly.^{54,55} The signal is then amplified (Pacific Instruments model 2A50, gain = 100, 150 MHz bandwidth), digitized by a transient recorder (Transiac, model 2001), and signal averaged by a DEC 11/73 microcomputer.

The reflectron mass spectrometer^{48–53} described above is not necessary for experiments on aluminum clusters, since conventional time-of-flight mass spectrometry readily achieves a mass resolution of 200, which is sufficient for the resolution of individual aluminum clusters and common impurities. The improved mass resolution (up to 1100 in our current design) and ability to investigate fragmentation processes provided by the reflectron mass spectrometer, however, will be very useful in investigations of other systems.

Resonant two-photon ionization spectra of Al₃ were obtained using a dye laser (Moletron, model DL-II) pumped by the second or third harmonic of a Q-switched Nd:YAG laser (Quantel, model 581-C) to excite the aluminum trimer to an excited electronic state, followed by photoionization with the output from a KrF excimer laser (Questek, model 2420, 248 nm). For these investigations the dye laser beam was directed down the molecular beam axis, and the KrF excimer laser beam crossed the molecular beam at right angles. Timing of the pulsed nozzle, the vaporization laser, the Nd:YAG-pumped dye laser and the excimer laser was controlled by a timing controller board which plugs into the Q-bus computer system, allowing 15 channels of digitally controlled delays, controlled in 250 ns increments (Codar Technology, Model 140 M-Timer). A higher resolution (1 ns) delay generator (Evans Electronics, Model 4141) was used to control the delay between the dye laser and excimer laser to within the limits of the excimer laser jitter.

III. RESULTS

A. Aluminum dimer

An experimental and theoretical controversy currently exists concerning the ground electronic state of diatomic aluminum. A magnetic deflection investigation⁵⁶ has clearly demonstrated the Al₂ ground state to be a triplet; if one assumes that the Al₂ ground state correlates to two ground state ($3s^23p$, 2p) separated atoms, this leaves only the $\pi_u^2(^3\Sigma_g^-)$ and $\pi_u^1\sigma_g^1(^3\Pi_u)$ states as candidates for the Al₂ ground state. Careful theoretical calculations show that the ground state is either $^3\Sigma_g^-$ or $^3\Pi_u$,^{57–60} and that these states are separated by only a few hundred wave numbers.^{59,60}

In previous gas-phase work on Al₃ an emission spectrum was observed in the 5650–6600 Å range which was assigned as either a $^3\Sigma_u^- - ^3\Sigma_g^-$ or $^3\Sigma_g^+ - ^3\Sigma_u^+$ transition.⁶¹ On the assumption that the lower state of this transition is the $\pi_u^2(^3\Sigma_g^-)$ term which is a candidate for the ground state of Al₂, a search for this band system was undertaken using resonant two-photon ionization of a jet-cooled beam of aluminum clusters. The photoionization laser used in this work was KrF (248 nm, 5.00 eV), which in combination with the dye laser provides a total energy in a 1 + 1 process of about 7.1 eV. Estimates of the Al₂ ionization potential are: 6.02,² 5.6,²⁷ 6.21 ± 0.21 ,⁶² and 6.0 ± 0.2 eV,⁶³ so this total energy should definitely be sufficient for ionization of the Al₂ mole-

cule. Despite a careful search for this transition, no resonant two-photon ionization spectra of diatomic aluminum were found. In matrix isolation absorption spectroscopy on aluminum clusters the 5650–6600 Å band system known in emission is conspicuously absent, suggesting that the $^3\Sigma_g^-$ lower state is not the ground state of diatomic aluminum. This is in agreement with sophisticated, highly detailed calculations.⁵⁹ Matrix isolation experiments^{64,65} reveal a structured band system near 400 nm that has been assigned⁵⁹ as a $^3\Pi_g - ^3\Pi_u$ transition, however. Again, we have searched for this transition by resonant two-photon ionization spectroscopy, without success. Presumably rapid predissociation competes with photoionization, preventing the observation of this transition. At this time no definitive experimental assignment of the ground state of Al₂ is possible.

B. Aluminum trimer: Spectral features

One of the beauties of resonant two-photon ionization spectroscopy coupled with time-of-flight mass spectrometry is that an entire mass spectrum is obtained on each shot. Thus, it is possible to monitor many cluster species during a given scan, and a search for transitions in the dimer, trimer, tetramer, etc., may be conducted simultaneously. During our search for the $^3\Sigma_u^- - ^3\Sigma_g^-$ band system of Al₂ in the 5650–6600 Å range we also recorded the aluminum trimer signal, and found the band system displayed in Fig. 2 quite by accident.

The spectrum displayed in Fig. 2 was recorded using a dye laser operating on the dyes coumarin 500, coumarin 540A, fluorescein 548, rhodamine 590, rhodamine 610, kinton red 62Q, and rhodamine 640, and is the result of several scans that have been pieced together. The dye laser fluence was not constant over all of these dyes, ranging from approximately 10 mJ/cm² at the red end of the spectrum to 2 mJ/cm² at the blue end. No attempt has been made to scale the intensity of spectroscopic transitions by normalizing to the

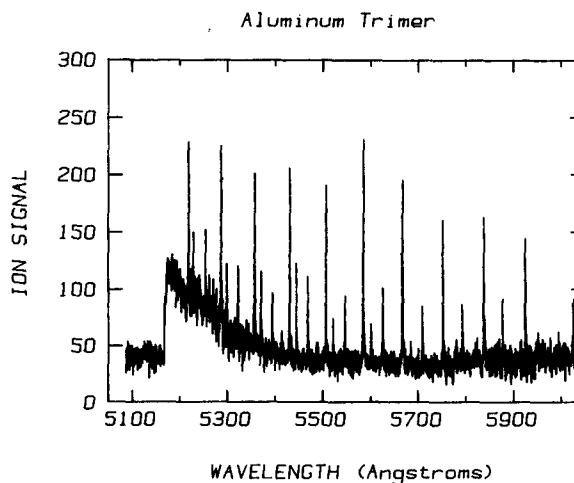


FIG. 2. Resonant two-photon ionization spectrum of Al₃, detected at mass 81 in the TOFMS. This is a combination of several spectral scans using various dyes, and has not been corrected for variations in the dye laser intensity. Corrected band intensities would show the bands at the red end of the spectrum much lower in intensity (about 20% of their intensity as plotted here).

intensity of the dye laser, so it is clear that the spectral features grow in intensity as one moves to the blue end of the spectrum. In all scans the photoionization laser was operated on KrF (248 nm), which was attenuated to give the optimum signal enhancement when the dye laser was tuned to a resonant absorption. As has been observed previously,⁵⁶ Al₃ is not a prominent feature in the mass spectrum of aluminum clusters and the Al₃⁺ signal observed in our mass spectrum is quite weak, even with the dye laser tuned to an absorption feature. In part, the apparent weakness of the Al₃ signal arises because we are using KrF radiation as our photoionization laser, and the common impurities Al₂O and Fe atoms both undergo resonant two-photon ionization at this wavelength. The mass spectrum obtained using KrF radiation is completely dominated by Al₂O, and when stock aluminum (6061 alloy) is used the iron atomic ion is also quite intense. Aluminum trimer is typically about a factor of 10 less intense than Al₂O under these conditions, even when the dye laser is tuned to a resonant absorption.

The observed resonant two-photon ionization spectrum of Al₃ is dominated by a single progression, for which eleven members have been identified. The bands are shaded to the red, and form a sharp bandhead toward the blue, indicating that the moments of inertia of the molecule increase upon electronic excitation. From the number of bands observed in the progression and the increase in intensity as one moves to the blue, it is evident that Al₃ undergoes a significant change in geometry upon electronic excitation, and that most of the change in geometry is associated with motion along one vibrational coordinate. The bandhead frequencies for this progression, along with the other observed bandheads are listed in Table I. Although poor Franck–Condon factors prevent an absolute vibrational numbering of the progression, the band positions are very well reproduced with $\omega'_1 = 273.2 \text{ cm}^{-1}$, $x'_{11} = -1.29 \text{ cm}^{-1}$ if the first observed band (at $16\,609.9 \text{ cm}^{-1}$) is assumed to be the origin. If subsequent work identifies this as the 1_0^n band, the anharmonic constant x'_{11} is unchanged, but the corrected value of ω'_1 will be $(273.2 + 2.58n) \text{ cm}^{-1}$. An absolute numbering of the observed progression would be possible if an isotopically modified form of triatomic aluminum were investigated, however, this is beyond our current budget and we have no desire to work with radioactive sources.

In addition to the main progression which dominates the spectrum, 9 of the 11 members of this progression show a weaker band $132.6 \pm 2.6 \text{ cm}^{-1}$ to the red of the major band. The fact that this weaker band occurs at an energy which is always 132.6 cm^{-1} to the red of the parent transition identifies these features as hot bands, arising from a vibronic level of the ground electron state lying 132.6 cm^{-1} above the vibrationless level. Although such an energy could arise in principle from a spin–orbit splitting, it is more likely that 132.6 cm^{-1} is the frequency of a bending mode in the ground electronic state. Hot bands built on the major bands at $16\,878.9$ and $16\,609.9 \text{ cm}^{-1}$ are presumably not observed because the parent transitions, located at the red end of the spectrum, already have poor Franck–Condon factors, and the hot bands built on these transitions will be even lower in intensity. Based on the intensity of the hot bands relative to

TABLE I. Al₃ bandhead frequencies and lifetimes.

Assignment	Bandhead frequency (cm ⁻¹)			Measured lifetime (μs)
	Measured ^a	Calculated ^b	Error	
Main Progression:				
1_0^n	16 609.9	16 607.2	2.7	...
1_0^{n+1}	16 878.9	16 877.8	1.1	97.3 ± 37.7
1_0^{n+2}	17 145.9	17 145.8	0.1	98.4 ± 42.9
1_0^{n+3}	17 410.7	17 411.3	-0.6	74.0 ± 15.5
1_0^{n+4}	17 672.1	17 674.2	-2.1	56.1 ± 10.5
1_0^{n+5}	17 934.1	17 934.4	-0.3	50.6 ± 3.1
1_0^{n+6}	18 192.9	18 192.2	0.7	44.8 ± 8.5
1_0^{n+7}	18 448.7	18 447.3	1.4	31.0 ± 1.4
1_0^{n+8}	18 701.2	18 699.9	1.3	...
1_0^{n+9}	18 949.2	18 949.9	-0.7	28.8 ± 3.4
1_0^{n+10}	19 193.8	19 197.3	-3.5	29.1 ± 5.2
Hot bands:				
1_1^{n+2}	17 011.5	17 013.2	-1.7	...
1_1^{n+3}	17 277.6	17 278.7	-1.1	...
1_1^{n+4}	17 539.3	17 541.6	-2.3	51.3 ± 8.8
1_1^{n+5}	17 801.9	17 801.9	0.0	40.7 ± 5.6
1_1^{n+6}	18 059.3	18 059.6	-0.3	...
1_1^{n+7}	18 317.0	18 314.7	2.3	35.2 ± 18.5
1_1^{n+8}	18 569.5	18 567.3	2.2	37.5 ± 8.1
1_1^{n+9}	18 818.7	18 817.3	1.4	25.6 ± 11.1
1_1^{n+10}	19 064.2	19 064.7	-0.5	21.7 ± 4.5
Combination bands:				
$1_0^{n+3} 2_0^1$	17 613.1	17 616.0	-2.9	...
$1_0^{n+4} 2_0^1$	17 879.1	17 878.9	0.2	39.3 ± 13.5
$1_0^{n+5} 2_0^1$	18 141.3	18 139.2	2.1	...
$1_0^{n+6} 2_0^1$	18 399.3	18 396.9	2.4	28.9 ± 12.8
$1_0^{n+7} 2_0^1$	18 651.0	18 652.1	-1.1	...
$1_0^{n+8} 2_0^1$	18 903.2	18 904.6	-1.4	28.7 ± 6.6
$1_0^{n+9} 2_0^1$	19 155.4	19 154.6	0.8	25.8 ± 8.4
Continuum edge	$19\,378 \pm 10$

^aThe measured bandhead positions are based on a calibration of the dye laser using the atomic aluminum two-photon absorptions $3s^2 4p ({}^2P_{1/2}, {}^2P_{3/2}) \leftarrow 3s^2 3p ({}^2P_{1/2}, {}^2P_{3/2})$, which occur in the $16\,400\text{--}16\,500 \text{ cm}^{-1}$ energy range. Measured bandhead positions are thought to be accurate to within $\pm 5 \text{ cm}^{-1}$ in absolute terms; energy differences are probably correct to within $\pm 2 \text{ cm}^{-1}$, with the exception of weak bands for which the bandhead is not clearly identified.

^bCalculated using $\nu = \nu_e + \omega'_1(v'_1 + \frac{1}{2}) + x'_{11}(v'_1 + \frac{1}{2})^2 + \omega'_2(v'_2 + \frac{1}{2}) - \omega''_1(v''_1 + \frac{1}{2})$. A least-square fit of these parameters yields $\nu_e = 16\,434.23 \pm 1.27 \text{ cm}^{-1}$, $\omega'_1 = 273.17 \pm 0.59 \text{ cm}^{-1}$, $x'_{11} = -1.29 \pm 0.05 \text{ cm}^{-1}$, $\omega'_2 = 204.74 \pm 0.94 \text{ cm}^{-1}$, and $\omega''_1 = 132.60 \pm 0.85 \text{ cm}^{-1}$. For this fit it was assumed that the $16\,609.9 \text{ cm}^{-1}$ band is the origin of the band system (i.e., $n = 0$ in the assignments given above).

the parent progression and assuming equal Franck–Condon factors for the parent transitions and the hot bands, a vibrational temperature of about $200\text{--}300 \text{ K}$ is achieved in these studies.

Finally, another set of weak bands are observed 40 to 60 wave numbers to the red of the members of the main progression. This separation is not constant, however, so this series of weak bands are not hot bands built on the stronger bands immediately to the blue. In fact, upon detailed comparison of the band positions of this series of weak bands and the

main progression it is evident that this series of bands cannot be assigned as hot bands terminating on the same upper states as the main progression, regardless of how the correspondence is made. The separation between this series of weak bands and the members of the main progression immediately to the red, however, is roughly constant at $204.7 \pm 3 \text{ cm}^{-1}$. Thus, the most compelling assignment of this set of bands is that they are combination bands involving one quantum of a 204.7 cm^{-1} vibration in the upper state along with varying numbers of quanta in the progression-forming mode. Alternatively, 204.7 cm^{-1} could be the spin-orbit splitting of the excited electronic state, although this value seems somewhat large based on the atomic $^2P_{3/2} - ^2P_{1/2}$ splitting of 112 cm^{-1} .⁶⁶

In addition to the discrete band system observed for Al_3 , an apparent continuum absorption gradually grows in as one moves toward the blue, beginning at about 5400 \AA . This continuum absorption is real, and is reproducible. At 5160 \AA the continuum absorption abruptly drops to zero, and no discrete transitions are observed to the blue of this wavelength. Such a continuum absorption is very uncommon in a jet-cooled molecule, especially in a triatomic molecule. In Sec. IV below an explanation of this continuum is proposed, along with an explanation of the anomalous lifetimes discussed below.

C. Aluminum trimer: Lifetime measurements

The lifetime of the electronically excited aluminum trimer may be measured by varying the time delay between the dye laser and the ionization laser, and determining how the trimer ion signal decays as this delay is increased. Experimentally, however, we are limited because we must fire the ionization laser when the clusters are in the ion source of the mass spectrometer. Since the clusters are traveling at a velocity of approximately $1.8 \times 10^5 \text{ cm/s}$, they traverse the ion source region in a period of about $15 \mu\text{s}$, and this limits our ability to measure long lifetimes. We have solved this problem by directing the dye laser down the molecular beam axis, so that the molecules may be excited long before entering the ion source. The ionization laser is set to fire when the largest concentration of aluminum trimers is present in the ion source, and the dye laser is scanned in time to provide the delay needed to characterize the decay of the electronically excited Al_3 . In this way we can measure excited state lifetimes as long as $300 \mu\text{s}$, limited only by the travel time of the clusters as they move from the nozzle to the ionization region of the mass spectrometer. Of course, systematic errors are possible with this method, particularly if the dye laser is either converging or diverging, or is poorly aligned with the molecular beam. Nevertheless, the method permits measurement of very long lifetimes which are difficult to determine by other methods.

Upper state lifetimes have been measured using this method for most of the observed transitions of Al_3 . The results are given in Table I. An example of the quality of data typically obtained for strong transitions is given in Fig. 3, which displays the exponential decay of the upper state of the 17934.1 cm^{-1} transition, with a fitted lifetime of $50.6 \pm 3.1 \mu\text{s}$. The lifetimes measured for electronically ex-

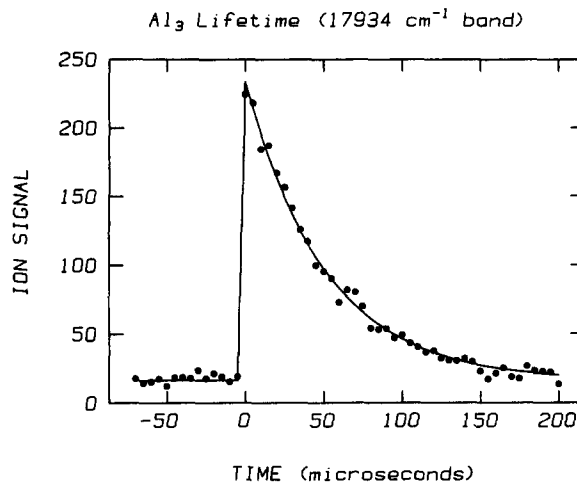


FIG. 3. Lifetime measurement of the upper state of the 17934 cm^{-1} band (points), fitted to a single exponential decay (solid line) with $\tau = 50.6 \pm 3.1 \mu\text{s}$. In this plot the abscissa refers to the time delay between the firing of the excitation dye laser pulse and the ionization excimer laser pulse. In the actual experiment the ionization laser is fired at a fixed time delay after the vaporization laser, and it is the excitation dye laser which is scanned in time.

cited Al_3 are very long, ranging from about $100 \mu\text{s}$ at the red end of the spectrum to about $25 \mu\text{s}$ at the blue end. Although it is possible that the measured lifetimes could be the radiative lifetimes of the various vibronic levels of the upper electronic state, such an assignment would require that the observed transitions be highly forbidden, with oscillator strengths f in the neighborhood of 5×10^{-5} . If this were the true oscillator strength of the transitions, it is doubtful that we would be able to observe them at all. An alternative explanation is provided in Sec. IV below.

In addition to these measurements of the lifetimes of the upper states of the discrete bands, we have made similar measurements with the dye laser tuned to arbitrary wavelengths within the continuum absorption. At dye laser frequencies in the range of 19000 to 19300 cm^{-1} , measurements of the upper state lifetime range from 35 to $24 \mu\text{s}$. It is most unusual for a continuum absorption in a small molecule such as Al_3 to possess such a long lifetime, since in most cases a continuum absorption indicates rapid fragmentation in the excited electronic state. In the case of Al_3 the continuum absorption is clearly not the result of direct excitation to a repulsive electronic state, as is often the case in small molecule spectroscopy. Moreover, the lifetime of the continuum absorption is identical (within experimental error) to the lifetime of the discrete transitions at comparable total energies. This unusual set of observations demands an explanation.

IV. DISCUSSION

In the preceding section several unusual aspects were noted in the spectrum of triatomic aluminum. First, and perhaps most unusual, is the observation of a continuum absorption which exhibits a long upper state lifetime. A spectral continuum such as this cannot result from direct excitation

to a dissociative electronic state, because the upper state lifetime of 24–35 μs is far too long to explain the continuum by lifetime broadening. Presumably, we are observing excitation into extremely high vibrational levels of an excited electronic state which is very different in geometry from the ground electronic state. In such a case Franck–Condon factors will favor excitation of extremely high vibrational levels, which may be so closely spaced as to be unresolved in our experiments. Aluminum trimer is calculated to have a ground electronic state which is nearly equilateral^{2,45,46} and to possess low-lying states which are linear in their equilibrium geometry.^{45,46} A transition from a nearly equilateral ground state to an excited state with a linear equilibrium geometry would favor very high excitations in the bending mode, and would probably excite the symmetric stretching mode as well. Indeed, at such high levels of excitation we are probably close to the dissociation limit, and the concept of normal modes is inappropriate for the proper description of the vibrational motions of the molecule at this level of excitation. A nearly equilateral to linear molecule transition would be expected to give an extremely congested, extensively perturbed spectrum which would grow in intensity as one moves toward higher photon energies. Assuming the spectral congestion to be so severe as to be unresolved, this is exactly what we observe in the rising continuum absorption.

In agreement with the expectations stated above, we observe a sharp cutoff in the continuum absorption at $19\,378 \pm 10\text{ cm}^{-1}$, consistent with the onset of dissociation above this energy. Presumably this is the dissociation limit of the excited electronic state, which was postulated to have a linear equilibrium configuration in the preceding paragraph. If this sharp cutoff does correspond to the dissociation limit of the excited state, then it is not surprising to observe a continuum absorption extending a few hundred wave numbers to the red, since the density of vibrational states will be very large this close to the dissociation limit. Moreover, many of these states will have significant Franck–Condon factors, given the large change in molecular geometry postulated above. If the dissociation products are ground state aluminum atoms and ground state Al₂, this places the dissociation energy of Al₃ at $D_0(\text{Al}_2\text{--Al}) = 2.40\text{ eV}$.

The dissociation energy measured above is considerably larger than the values calculated by *ab initio* theory: 1.67,² 1.93,⁴⁵ and 1.55 eV.⁴⁶ A recent measurement of the dissociation energy of the aluminum trimer cation (Al₃⁺) by Hanley *et al.* using collision-induced dissociation techniques has provided a value of $D_0(\text{Al}_2^+ \text{--Al})$ of $1.12 \pm 0.35\text{ eV}$.⁶³ In combination with the estimated ionization potentials of Al₂ and Al₃ of 6.21 ± 0.21 ⁶² and $6.46 \pm 0.04\text{ eV}$,⁶² respectively, this yields a value of $D_0(\text{Al}_2\text{--Al})$ of $1.37 \pm 0.60\text{ eV}$. Alternatively, Hanley *et al.* have measured $D_0(\text{Al}^+ \text{--Al}_2)$ to be $1.30 \pm 0.35\text{ eV}$,⁶³ which in combination with the estimated ionization potential of Al₃⁶² and the known atomic ionization potential of 5.984 eV⁶⁶ yields a value of $D_0(\text{Al}_2\text{--Al}) = 1.78 \pm 0.39\text{ eV}$. Hanley *et al.*⁶³ have resolved the discrepancy between these values with the assumption that the dissociation of Al₃⁺ to ground state Al⁺ and Al₂ is a spin-forbidden process, and dissociation into these fragments will not occur until enough energy is available to produce Al₂ in

an excited singlet state, located approximately 0.4 eV above the ground state of Al₂. In any case, the dissociation threshold measured in this work is significantly higher than any of the available theoretical or experimental estimates.

One explanation for this discrepancy is that the dissociation limit determined here leads to electronically excited fragments. The lowest excited electronic state of the aluminum atom lies at 3.14 eV,⁶⁶ so atomic excitation is out of the question. On the other hand, calculations indicate the existence of numerous low-lying electronic states of Al₂,^{57–59} many of which could be candidates for the dissociation limit. This explanation of the discrepancy between our observed dissociation limit and those calculated or derived from other experimental information, however, leaves unresolved one major question: How is it possible that Al₃ can be excited to an energy within 100 cm^{-1} of a dissociation limit corresponding to *electronically excited fragments*, and yet remain bound for a lifetime of about 25 μs ? At this level of excitation in the excited electronic state the molecule is certainly undergoing large-amplitude vibrations which sample a large configuration space. With the number of potential energy surfaces suggested for Al₃ one would expect many conical intersections coupling one state to another within the large configuration space sampled, and dissociation on a lower surface should occur readily. Regardless of whether Al₃ is excited to a doublet ($S = 1/2$) or quartet ($S = 3/2$) state, dissociation to a ²P aluminum atom and ground state ($S = 1$) Al₂ should be spin allowed, so there appear to be no conservation rules preventing dissociation. With these facts in mind, one would expect the dissociation threshold measured in the current work to be the dissociation limit for production of ground-state fragments. Further work is needed to resolve the discrepancy between this result and previous investigations.

In addition to the continuum absorption, which halts abruptly at $19\,378 \pm 10\text{ cm}^{-1}$, the discrete band system also halts abruptly at this energy. The main progression of the discrete system is quite regular up to this cutoff, and we have carefully looked for the next member of the progression, which is calculated to occur at $19\,442.2\text{ cm}^{-1}$ on the basis of the least-squares fit given in Table I. Despite careful adjustment of the time delay between the dye laser and the excimer laser, no resonance-enhanced Al₃⁺ ion signal could be observed within 50 cm^{-1} of this frequency. On the basis of the pulse durations of our lasers this places the lifetime of the unobserved vibronic level below 10 ns. This indicates that predissociation is occurring in the discrete band system at energies above $19\,378\text{ cm}^{-1}$, on a time scale faster than 10 ns. Although the hot band expected 132.6 cm^{-1} to the red of this expected transition should occur at a transition frequency below the $19\,378\text{ cm}^{-1}$ cutoff, it too is unobserved. This confirms the assignment of the hot band progression, since it is the energy of the upper state rather than the transition frequency which determines whether or not predissociation will occur. The first unobserved combination band is calculated to occur at $19\,402.1\text{ cm}^{-1}$, which is above the predissociation cutoff, thereby explaining its absence from our spectrum.

The remaining anomaly yet to be explained is the long

lifetime of both upper states, along with the observation that the two lifetimes are identical within experimental error. These observations are nicely explained by postulating that the discrete state is undergoing nonradiative decay to the quasicontinuum of the state responsible for the continuum absorption, and that it is the lifetime of this latter state which is being measured in our experiments. This mechanism requires nonradiative decay of the discrete state to occur on a time scale of 10 ps to 10 ns. A faster time scale would lead to lifetime broadening of the discrete bands beyond that which we observe, while a longer time scale would lead to biexponential decays, which are also not evident in our data. The mechanism invoked here also nicely explains why both the discrete and the continuum absorptions terminate abruptly at 19 378 cm⁻¹. Above this energy the continuum absorption leads directly to dissociation, and the discrete bands undergo rapid (< 10 ns) predissociation by nonradiative decay into the dissociative continuum of the state responsible for the continuum absorption.

V. SUMMARY

An optical spectrum has been observed for the aluminum trimer, Al₃, by resonant two-photon ionization spectroscopy. As opposed to *s*-bonded metal trimers such as Na₃ and Cu₃, this is the first *p*-bonded metal trimer to be spectroscopically observed in the gas phase. The spectrum is characterized by an extended vibrational progression in a vibrational mode with $\omega'_1 = 273.2$ cm⁻¹ and $x'_{11} = -1.29$ cm⁻¹. Hot bands are also observed which demonstrate the presence of a ground state vibronic level 132.6 cm⁻¹ above the zero-point level. A series of combination bands are also observed, corresponding to a second vibrational mode of the excited electronic state with a vibrational frequency of $\omega'_1 = 204.7$ cm⁻¹.

In addition to the discrete band system, a continuum absorption is also observed. This is most unusual for a jet-cooled triatomic molecule. More surprising yet is the observation that the upper state of the continuum absorption exhibits a long lifetime of 24–35 μ s. It is argued that this continuum absorption corresponds to direct excitation extremely high in the potential surface of an excited electronic state of Al₃ which is grossly distorted relative to the ground state. A geometry change from near-equilateral in the ground state to linear in the excited state is suggested to account for the apparent continuum absorption. At slightly higher energies both the continuum and discrete absorption systems abruptly cease, and no absorptions are observed at energies higher than 19 378 cm⁻¹. This is interpreted as the dissociation limit of the excited state responsible for the continuum absorption.

The lack of discrete bands to the blue of 19 378 cm⁻¹ is evidence that the excited state responsible for the discrete transitions is coupled to the excited state responsible for the continuum absorption, and is predissociated above this energy. The long lifetimes of the upper states of the discrete transitions are indicative of an intimate mixing of these levels with high vibrational levels of a lower electronic state, presumably the state responsible for the continuum absorption. The observation that the upper states of the discrete transi-

tions exhibit identical lifetimes (within experimental error) as the upper state of the continuum absorption also argues for an intimate coupling between these electronic states.

Work is currently in progress to improve the Al₃ signal intensity, and if this is successful a high-resolution spectroscopic investigation will be undertaken, with the aim of determining the geometrical structure and electronic state symmetry of triatomic aluminum, in both the ground and the excited electronic states.

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