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Electron Stimulated Desorption of the Metallic Substrate at Monolayer Coverage: Sensitive Detection via 193 nm Laser Photoionization of Neutral Aluminum Desorbed from $CH_3O/Al(111)$*

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Electron Stimulated Desorption of the Metallic Substrate at Monolayer Coverage: Sensitive Detection via 193 nm Laser Photoionization of Neutral Aluminum Desorbed from $CH_3O/Al(111)$[*]

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Abstract. A fortuitous overlap between the gain profile of the 193 nm ArF excimer laser and the Al autoionizing transition $^2S_{1/2}$ (51753 cm^{-1}) <— $^2P^0_J$ (J=1/2,3/2; 0,112 cm^{-1}) has been exploited in the direct observation of substrate metal atoms in an electron stimulated desorption (ESD) process from the monolayer adsorbate system $CH_3O/Al(111)$. The identity of the mass 27 photoion was established as Al^+ by (1) isotopic substitution of ^{13}C in the methanol employed for methoxy formation, and (2) tunable laser scans utilizing the ^2D_J (J=3/2, 5/2) intermediate levels at ~32436 cm^{-1} and a 248 nm ionization step. An ESD yield of ~3x10^{-6} Al atoms/(electron at 1 keV) was established by comparison with a sputtering experiment in the same apparatus (Ar^+, 3.6 k eV). Velocity distributions measured for the desorbed Al species showed some differences in comparison with methoxy velocity data: a slightly lower peak velocity [800 m/s (Al); 1100 m/s (methoxy)] and a significantly less prominent high-velocity component.

1. Introduction

This paper is a summary of recent experiments by our group on the detection of clearly measurable Al^+ photoion signal resulting from the laser-ionization of neutral species desorbed in an ESD process from the methoxy/aluminum [$CH_3O/Al(111)$] system. Our previous measurements on $CH_3O/Al(111)$ [1, 2] established the utility of 193 nm nonresonant photoionization for the measurements of yields and velocity distributions of CH_3O resulting from ESD with 3 keV primary electrons. The present work demonstrates the desorption of a substantial yield of substrate atoms from a single-crystal metallic system having only monolayer methoxy coverage. Fuller accounts of these experiments have been prepared for submission elsewhere.

◁ Fig. 1

2. Apparatus and Procedures

For the present measurements, a high-sensitivity laser-ionization mass spectrometer built in our laboratory [3, 4] was equipped with an electron gun and focusing-lens stack, making either electron or ion bombardment of the sample possible while maintaining the photoion extraction conditions invariant. For ESD experiments, primary electron energies in the hundred volt to kilovolt range were conveniently available; 1 keV was employed in the present measurements. The extraction optics (and other elements) were verified to be operating at potentials low enough for any extraneous electron current arriving at the sample to be negligible. The electron gun could be operated in a pulsed mode (≥ 100 ns) for obtaining time-of-flight (TOF) velocity distribution data or with long pulses (averaging ~1 μA in a 1 mm spot) in order to establish steady-state conditions for yield determinations. Sample preparation involved cleaning via standard heating and sputtering cycles with verification by AES, XPS, and LEED. Dosing with excess methanol (≥50 L) then produces a monolayer methoxy coverage; supporting evidence and references have been summarized previously [1, 2]. The laser excitation scheme is illustrated in Fig. 1. For velocity distribution and yield measurements, 193 nm light from an ArF excimer laser was used under "soft focus" conditions (0.8 x 2.2 mm spot, 20 ns pulse). In Al resonance-ionization experiments, crystal second-harmonic doubling of dye laser output was synchronized with 248 nm radiation from a second excimer for the ionization step.

3. Results and Discussion

Most of the data on neutral Al ESD was obtained in the laser intensity region ≤ 5 MW/cm^2 where background signal from other species is small, in contrast to the regime ≥ 100 MW/cm^2 where the methoxy species is easily ionized and its photofragment ions appear. Two definitive tests established the identity of the mass 27 neutral desorbate: (1) expected mass shifts when CH_3O was prepared by dosing with ^{13}C methanol, and (2) the resonance ionization experiment depicted in Fig. 2, where ~309 nm tunable light populated excited levels which were efficiently photoionized by 248 nm photons (~14 MW/cm^2). Despite some nonresonant signal from the intense 248 nm light, characteristic neutral Al resonances are clearly observed. Additional experiments established the following facts. (1) No mass 27 signal was observable when the ESD experiment was performed on clean Al(111). (2) Subsequently, the Al signal appeared clearly upon deposition of a saturation methoxy coverage. (3) Pyrolysis at 600K, a process known to leave only surface oxide and carbide species [5] caused a drastic reduction in the mass 27 ESD.

Velocity distribution data, shown in Fig. 3, was obtained via TOF from sample to photoionization volume (2.2 and 4.4 mm paths) with 193 nm radiation and electron pulse lengths of ~1 μs. The peak velocity of 800 m/s was somewhat less than the corresponding value of 1100 m/s observed for methoxy desorption from Al(111).

◁ Fig. 2

◁ Fig.3

The Al signal is better represented by a narrow parametric model (Boltzmann) rather than the "planar barrier" formulation containing some high-energy component, needed to fit typical CH_3O desorption distributions [2].

An absolute yield for Al neutral desorption was reliably determined through a calibration experiment in which aluminum atoms were sputtered into the gas phase with a known yield, for Al(111), of $Y_s = 2.2$ atoms/(Ar^+ ion at 3.6 keV) [6]. The velocity distribution needed to convert the density data proportional to the detected signal to flux data proportional to yields was measured (Fig. 3) for ESD, and modelled by an accurate and established formulation [7] for sputtering. In the ESD experiment, The neutral Al density, n, in the ionization volume is given as $n = I_e YG/(2v_m\sqrt{\pi})$, where I_e is the current of bombarding electrons (e^-/sec), $v_m = \sqrt{(2kT/\text{mass})}$, i.e., the Boltzmann peak velocity (a fitting parameter here), and $G = \langle\cos\theta/R^2\rangle$ a geometric average over the takeoff angle θ and the sample-to-volume distance R. A corresponding formula applies to the sputtering data, with the factor $2\sqrt{\pi}$ replaced by 4, I_e replaced by I_s, the ion current, and Y by Y_s, given above. Also, v_m is replaced by $v_b = \sqrt{(2E_b/\text{mass})}$, E_b being represented by the heat of sublimation of aluminum, 3.36 eV. Assuming the factor G to be the same in both experiments, we calculate $Y = 3.2 \times 10^{-6}$ Al atoms/(1 keV electron) for the ESD process. The latter is significantly smaller than the methoxy yield ($\sim 10^{-3}$ at 3 keV [1, 2]), but larger than the corresponding measured ESD yield of ions ($\sim 10^{-6}$ protons/(3 keV electron)).

Our attempts to observe the parent neutral desorbate leading to the observed Al^+ photoions have thus far been unsuccessful, despite the ability to utilize a large range of laser intensities from ~100 MW/cm^2 to 0.1 kW/cm^2. However, some indication that the initial desorbate may be molecular is contained in laser saturation curves, i.e., Al^+ photoion signal versus laser intensity. The ESD process is compared with sputtering, where the released species is overwhelmingly atomic. The ESD signal is observed to decrease more rapidly than that from sputtering as the laser intensity is reduced. Thus, a photodissociation scheme AlX ->Al ->Al^+ is suggested, in which the parent molecule, AlX, is laser-dissociated to Al atoms which subsequently ionize efficiently due to the 193 nm overlap with a 1-photon autoionizing transition (see Fig.1). Quantitative modelling is in progress. It can be noted that the $AlOCH_3^+$ species is known in SIMS monitoring of the CH_3O/Al(111) system [8]. The Al-O bond in the neutral species $AlOCH_3$ has recently been determined to be 5.44 ± 0.1 eV by G2 ab initio theory [9]. Calculations at a lower accuracy level with the methoxy species bound on various clusters $(Al)_n$ confirm the picture of a strong Al-O bond [9].

Finally, we note that ESD followed by 193 nm laser mass spectrometry on the analogous system - water-dosed Al(111) - exhibits numerous easily detectable neutral aluminum molecular species as indicated in Fig. 4. The AlOH parent is seen, as well as various AlH_n fragments, the latter being expected in view of the recent observation of electron-bombardment fragments from AlH_3 and Al_2H_6 thermally desorbed from hydrogen-dosed aluminum [10]. Consequently, the $AlOCH_3$ neutral

◁ Fig. 4

desorbate (or other parent precursor) may be detectable in another wavelength range where the photodissociation process may be less dominant.

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Figure Captions

Fig. 1 Energy level diagram for the neutral aluminum atom. Autoionizing transitions are shown on the left and the resonance ionization pathways on the right.

Fig. 2 Resonance ionization spectrum of Al atoms detected in the ionizing sequence of Fig. 1. Resonances in the Al photoionization spectrum occur at the expected ultraviolet wavelengths, generated by crystal frequency doubling.

Fig. 3 Velocity distributions obtained for the desorbed neutral Al species by 193 nm photoionization. Data are for two flight distances - open points: 2.2 mm, solid points: 4.4 mm.

Fig. 4 Photoionization mass spectrometry at 193 nm on neutral species desorbed by 1 k eV electrons from slightly oxidized, water-dosed Al(111). Laser intensity was ~1 MW/cm^2.

Aluminum: Electronic Energy Levels
Atom

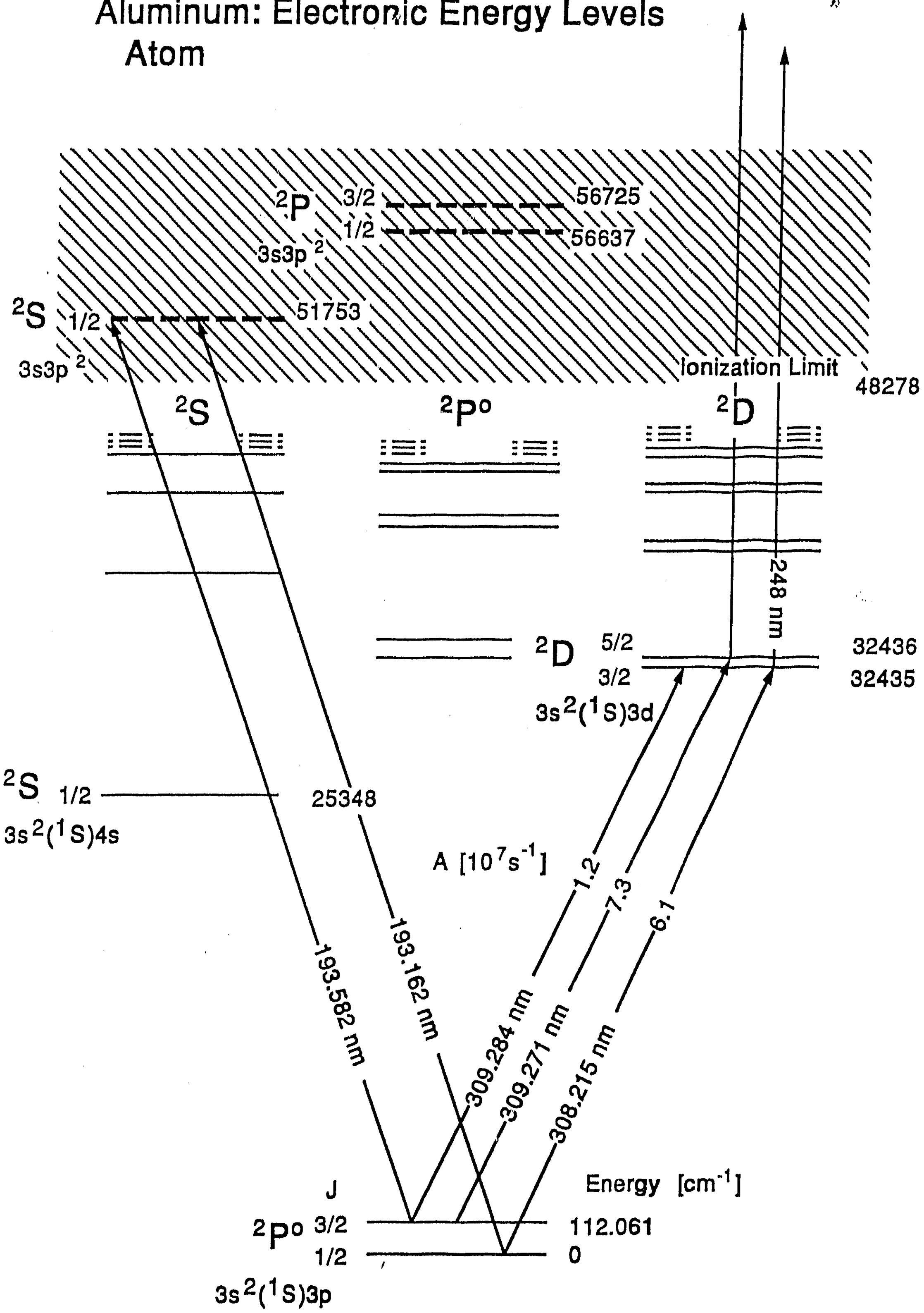

Fig. 1

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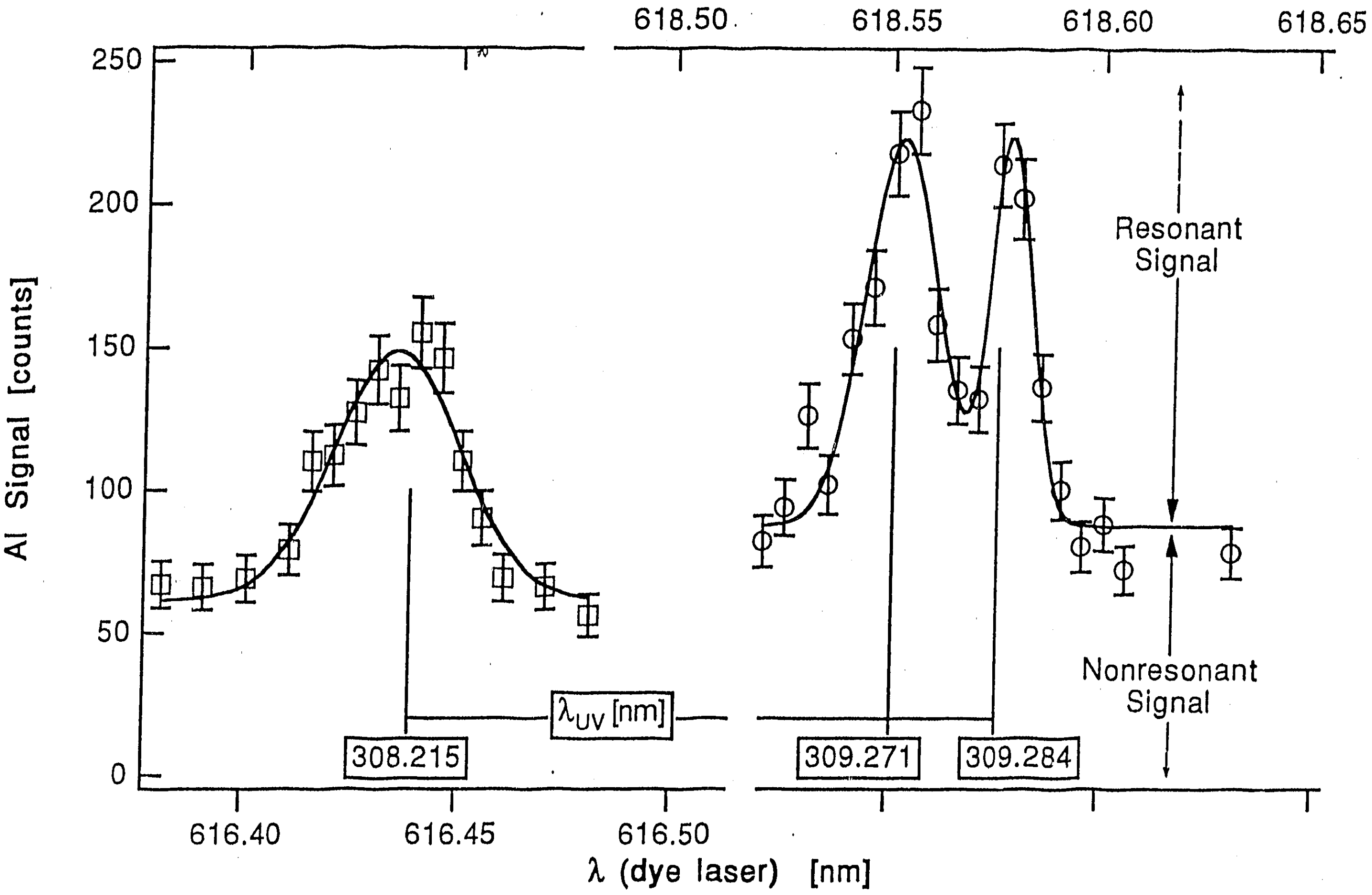

Fig. 2

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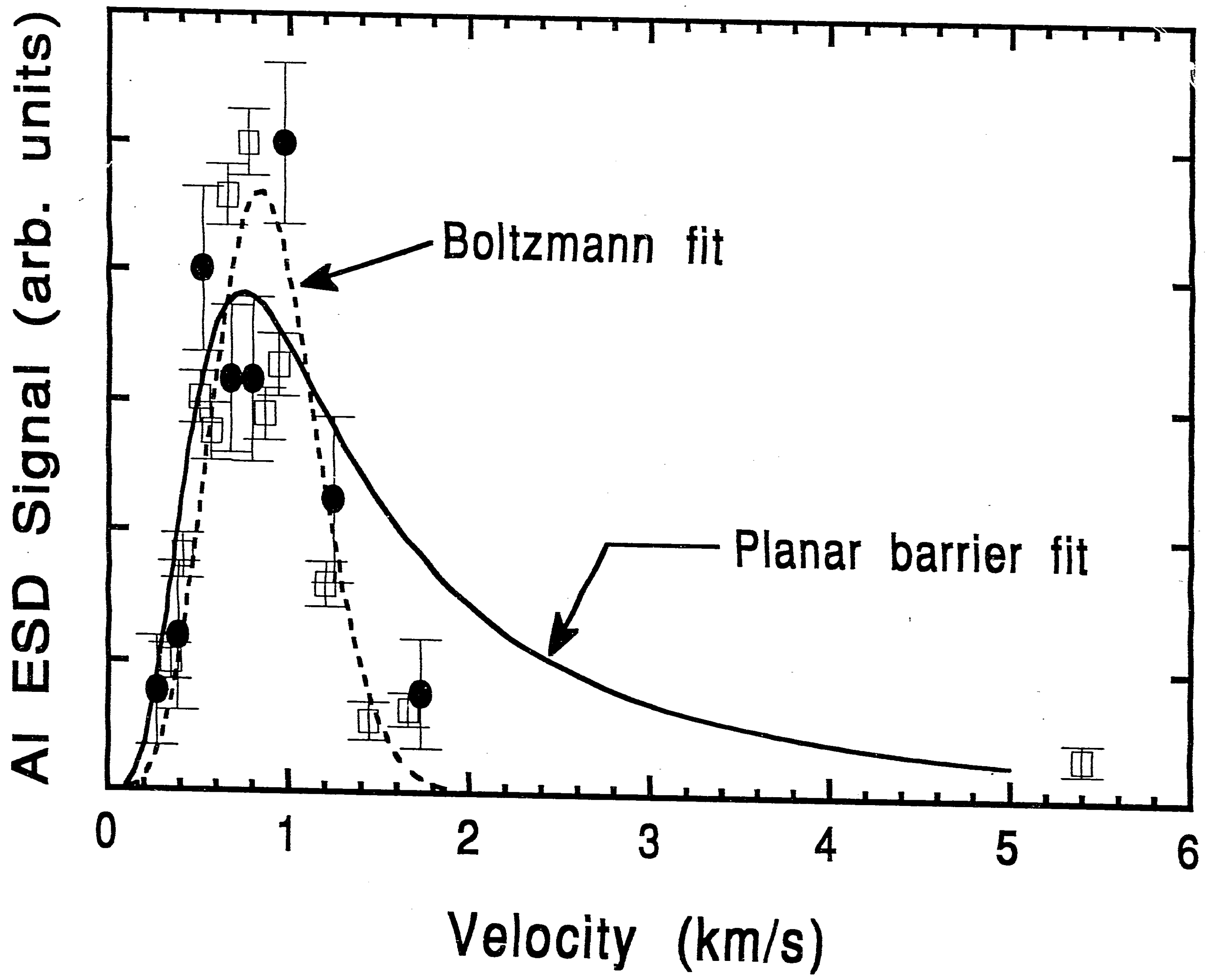

Fig. 3

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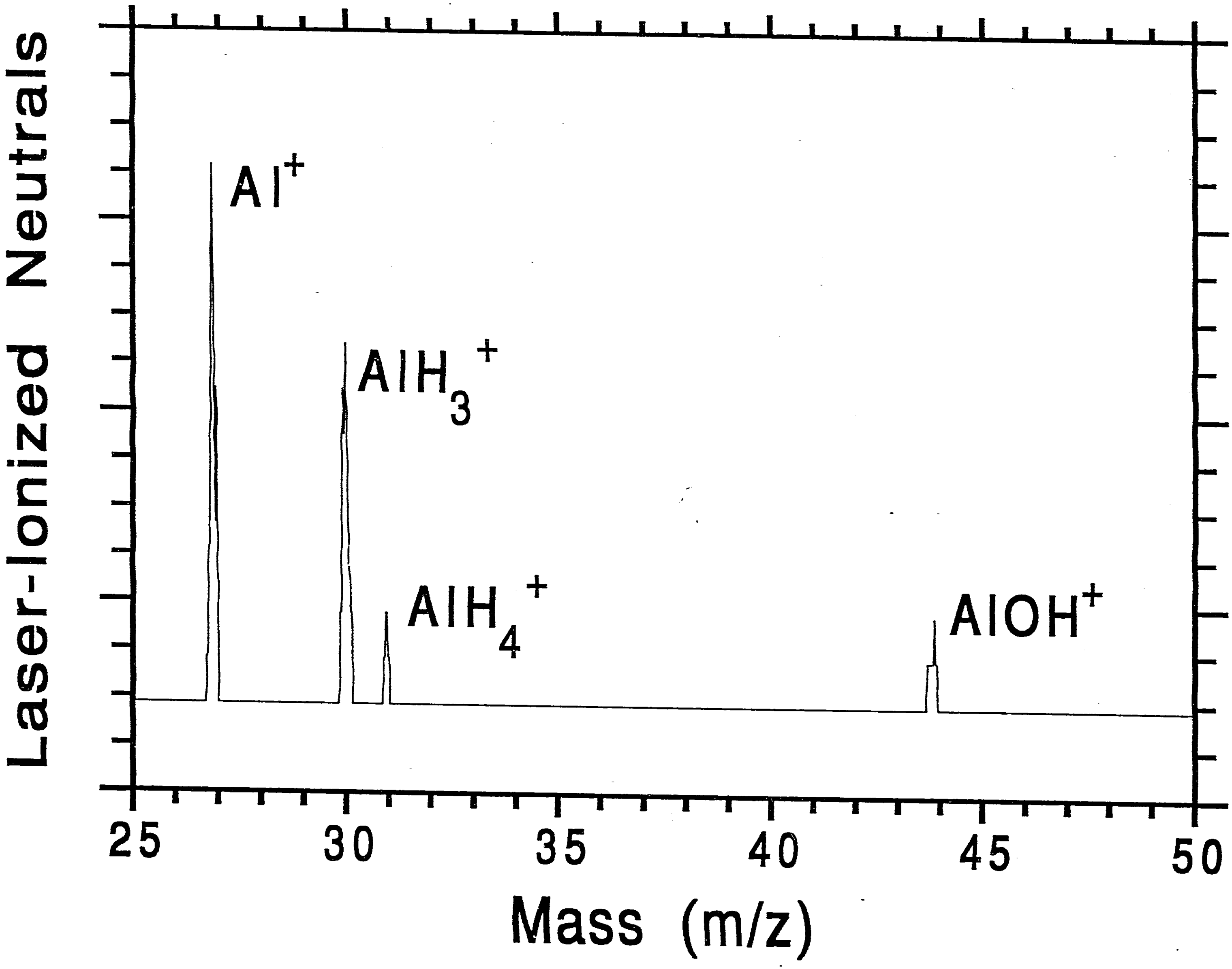

Fig. 4

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