

We have seen that only the trace model (F) is capable of reproducing both measurements, spectrum, and dielectric coefficient. As long as we restrict our attention to analytical models of the form of Eq. (1), which is generally accepted,⁸ the only adjustable parameter other than λ is the range ρ . If ρ is increased, more narrow-banded spectra result, and *vice versa* (not shown). If we choose $\rho = 0.72a_0$, a coefficient λ of $1430a_0^3$ will give an acceptable fit of both the spectrum and the virial coefficient. However, a ρ of $0.68a_0$ cannot be made to fit both measurements with the same λ , and is therefore not an acceptable model. Similarly, a ρ of $0.80a_0$ appears to be unacceptable. The analytical model [Eq. (1)] appears to be sufficient because only a very narrow range of r values (between 3 and 5 Å) shape the spectra.⁸

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Electron affinities of B, Al, Bi, and Pb

C. S. Feigerle, R. R. Corderman,^{a)} and W. C. Lineberger^{b)}

Department of Chemistry and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

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The ability to determine atomic electron affinities experimentally has been greatly enhanced by the availability of laser light sources.^{1,2} The quantitative state of such measurements has been recently reviewed³⁻⁵ and these reviews make it clear that additional versatility in ion production methods is badly needed to extend such data. In this note, we report the photoelectron spectra of B^- , Al^- , Bi^- , and Pb^- and the electron affinities of the corresponding neutrals. These ions were all produced using a simple sputter ion source,⁶ and represent elements of the main body of the Periodic Table whose electron affinities were among those least well known. A 1D electronic excited state of Al^- was observed. A subsequent detailed publication⁷ will deal with electron affinities of the transition metals.

The experimental apparatus has been described in detail previously.⁸ A 680 eV mass analyzed negative ion beam is crossed by the focused intracavity beam of an Ar II laser operating at either 488 or 457.9 nm. Electrons photodetached into a small solid angle are energy analyzed (resolution ~ 60 meV) and counted to obtain a photoelectron spectrum.

The sputter ion source used in these experiments is

a scaled-down version of a Middleton-type sputter source developed for use with Tandem van de Graff accelerators.⁹ Cesium positive ions are produced by surface ionization, accelerated to 4 keV, and focused onto an appropriate metal target. The metal target was either in the form of a flat disk with a small (1 mm) hole or a cone with a 1 mm diam hole at the apex, from which negative ions were extracted. With positive ion beam currents of ~ 100 μA , sputtered negative ion beam currents of the atomic metal negative ion of 5–100 pA were easily attained.

The absolute photodetached electron energy scale is determined by simultaneous photodetachment of the ion of interest and an ion whose E. A. is known, in this case O^- . Depending upon the complexity of the spectra involved, electron affinities and excited state locations can be determined to accuracies⁸ of ± 0.003 to ± 0.030 eV.

A 10 pA beam of Pb^- was obtained by sputtering a lead cone. The ground state of Pb^- is expected to be a $6p^3$ 4S state, with a possible 2D excited state. From the ground state of the negative ion, photoelectron transitions are possible to the $^3P_{0,1,2}$ states of neutral

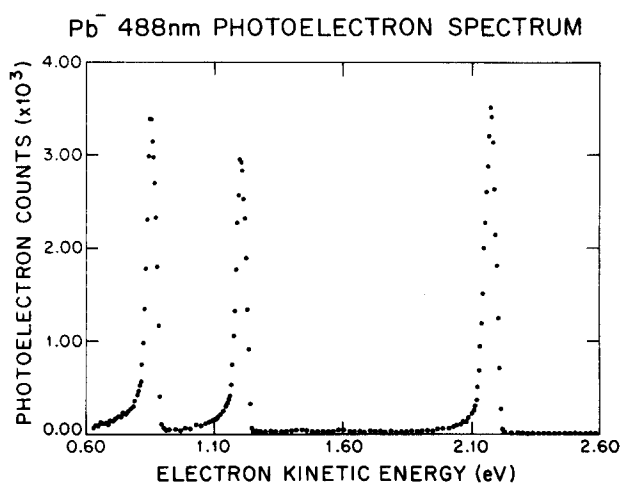


FIG. 1. Photoelectron spectrum of Pb⁻ ions, obtained with 488 nm (2.540 eV) photons. The three peaks correspond (right to left) to transitions from the ⁴S state of Pb⁻ to the ³P₀, ³P₁, and ³P₂ states of Pb.

lead. These transitions are observed in the photoelectron spectrum of Pb⁻ obtained with 488 nm photons (2.54 eV), shown in Fig. 1. The three peaks are assigned to transitions from the ⁴S state of the negative ion to the ³P_{0,1,2} fine structure levels of the neutral on the basis that their separations agree with the known neutral splittings to within 2 meV. From this spectrum the electron affinity of Pb is found to be 0.365 ± 0.008 eV. There is no evidence in the photoelectron spectrum for the existence of the ²D state of Pb⁻. The intensities of the transitions to the ³P_{0,1,2} fine structure levels are all comparable, in contrast with the 1:3:5 ratio expected¹⁰ in the case of LS-coupled states.

The most noteworthy previous determination of the electron affinity of Pb was a photodetachment measurement of Kaiser.¹¹ This measurement was a photodetachment threshold study which could not, because of light source limitations, extend below 0.5 eV. This photon energy limitation afforded two alternative sets of conclusions, that E.A. (Pb) was either 0.25–0.35 or 1.2 eV; the higher value was chosen by Kaiser and the existence of a ²D excited state of Pb⁻ was postulated. The present experiment shows unequivocally that the alternative interpretation of the Kaiser data is the correct one.

In the case of Bi⁻, comparison with the isoelectronic Po suggests that only the 6p⁴ ³P₂ state should be stable. From this state, transitions to the ⁴S and ²D_{3/2} states of Bi are possible. Both of these transitions are observed in the 457.9 nm spectrum of sputtered Bi⁻ ions, resulting in an electron affinity for Bi of 0.947 ± 0.010 eV. This result is in qualitative agreement with earlier but less accurate surface ionization¹² (1.1 eV) and photodetachment¹³ (0.9–1.2 eV) experiments.

Insertion of an aluminum target produces beams of

Al_n⁻, n = 1...4. The ground state of Al⁻ is expected to be 3p² ³P_{0,1,2} with extrapolated spin-orbit splittings³ of 26 and 50 cm⁻¹. In addition, a ¹D₂ excited state is expected³ to be bound. Transitions from both of these states to the ground state of Al were observed in the 488 nm photoelectron spectrum. Taking into account the unresolved estimated fine structure intervals, the electron affinity of Al is found to be 0.442 ± 0.010 eV; the excitation energy of the Al⁻ ¹D₂ state is found to be 0.332 ± 0.010 eV. These results are in reasonable accord with earlier photoelectron data³ (0.46 ± 0.03 and 0.34 ± 0.03 eV respectively) and the field ionization studies¹⁴ of Oparin *et al.*

The last ion studied in the series was B⁻. Insertion of a LaB₆ target in the sputter source produced an intense beam of BO⁻, with small (5–10 pA) currents of B⁻ and B₂⁻ ions. The ground state of B⁻ is expected to be ³P_{0,1,2}, with very small (<10 cm⁻¹) spin-orbit splittings. From this negative ion state, one expects transitions to the ground ²P state of B. While extrapolations indicate that it is possible that a ¹D state of B⁻ is stable, the photoelectron spectrum of B⁻ indicates that only the ³P state is bound and yields an electron affinity of B of 0.278 ± 0.010 eV. This result is in accord with the less accurate (0.28 eV) photodetachment data reported earlier.³

In summary, we have utilized a new sputter source of negative ions to obtain electron affinities of a number of electron deficient elements for which accurate electron affinities have not previously been available. These data reinforce affinity trends reported earlier³ and emphasize the ubiquity of excited states of negative ions.

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²Present address: Department of Energy and Environment, Building 480, Brookhaven National Laboratory, Upton, NY 11973.

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van der Waals molecules and the mechanism of dimer formation in jet-cooled CF_3NO

Benjamin M. DeKoven^{a)} and Donald H. Levy

The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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We have recently completed a study of the fluorescence excitation and dispersed fluorescence spectra of the molecule CF_3NO .¹ Under ordinary conditions CF_3NO is a blue gas, and its color is due to a very complex and extensive absorption spectrum that begins in the near infrared and extends through the long wavelength part of the visible. This very dense spectrum is in large part due to transitions arising from excited vibrational and rotational levels that are heavily populated at room temperature, and the spectrum is greatly simplified by cooling in a supersonic expansion. The spectroscopic work on CF_3NO itself has been described in another paper.¹

In the course of the work on CF_3NO we observed spectral features which we believe are due to van der Waals molecules consisting of one or more helium atoms bound to a CF_3NO molecule. Moreover, the relative intensity of these features suggest that dimers or higher polymers of CF_3NO are being formed in the supersonic expansion. This note is a description of these weakly bound complexes.

The supersonic free jet was formed by expanding a mixture of a small amount of CF_3NO in a helium carrier gas through a 25 micron nozzle. The total upstream pressure was ~ 60 atm, and the details of the supersonic jet have been given elsewhere.² The spectrum was excited with a pulsed Nd:YAG pumped oxazine 725 dye laser (Quanta-Ray) which produced 10–15 mJ pulses at a repetition rate of 10 Hz. Fluorescence was either detected directly (the fluorescence excitation spectrum) or dispersed with a 1 m monochromator and then detected (the dispersed fluorescence spectrum) using uncooled photomultipliers and gated integration. The details of the light collection and dispersing optics have also been described previously.^{2,3}

In Fig. 1 we show a part of the fluorescence excitation spectrum of CF_3NO and its helium van der Waals molecules. The entire fluorescence excitation spectrum is dominated by a long progression in ν_{12} , the CF_3 torsional vibration. The feature shown in Fig. 1 is the transition at 14301 cm^{-1} from the zero point level of the

ground electronic state to the third excited torsional vibrational level in the excited electronic state (12_0^3). It is a typical member of the torsional progression.

The top trace in Fig. 1 was taken with a 0.5% mixture

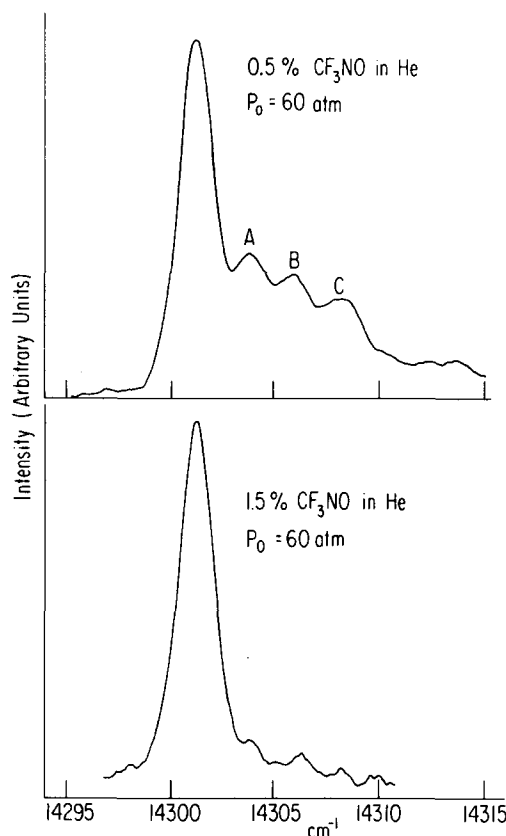


FIG. 1. A portion of the supercooled CF_3NO fluorescence excitation spectrum near 14300 cm^{-1} showing CF_3NO van der Waals complexes (features A, B, and C) with helium is shown. The upper and lower traces correspond to 0.5% and 1.5% $\text{CF}_3\text{NO}/\text{He}$ mixtures, respectively, the total pressure being ~ 60 atm. The spectra are normalized so that the main band due to uncomplexed CF_3NO has the same intensity in both traces.