Single- and Multiphoton Infrared Laser Spectroscopy of Sb^-: A Case Study

Michael Scheer and Harold K. Haugen*
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

Donald R. Beck
Physics Department, Michigan Technological University, Houghton, Michigan 49931
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A combination of single- and multiphoton tunable infrared laser experiments is utilized to accurately and conclusively determine the bound terms and fine structure of $Sb^-(5p^4)$. The $^3P_2$ binding energy is determined to be 8447.86(15) cm^{-1} (electron affinity of antimony) and the previously unobserved $^3P_1$, $^3P_0$, and $^1D_2$ levels are found at 2684.37(15), 2800.8(6), and 7392.55(15) cm^{-1} above the $^3P_2$ ground level, respectively. Relativistic configuration interaction calculations predict these splittings to be 2516, 2831, and 7628 cm^{-1}. Widths and shapes of resonances observed in two-photon detachment yields are modeled on the basis of calculated hyperfine structure constants. [S0031-9007(97)04614-0]

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The spectroscopy of negative ions has been an area of considerable interest for the past two decades (for recent reviews, see Ref. [1]). Recently, multiphoton techniques have been successfully established in this field. Studies either addressed fundamental optical phenomena since negative ions, due to their short range potentials, represent qualitatively different targets for strong-laser-fields studies [2], or they were aimed at the elucidation of negative ion structure. Both resonant structures in the continuum of negative ion species [3] as well as bound excited states [4,5] have been probed via multiphoton schemes. The energy levels of a negative ion below its first detachment limit almost always refer to the terms and fine structure of the same (ground state) electronic configuration and are still only poorly determined in many negative ion systems. Optical transitions between such levels are forbidden in a conventional single photon electric dipole scheme as a result of the parity selection rule. However, a simultaneous absorption of two photons would be allowed in an electric dipole interaction and has been demonstrated in negative ions for the case where the two photons have different energies and are absorbed via a Raman coupling scheme [4]. In addition, small probabilities exist for single-photon transitions of magnetic dipole (M1) or electric quadrupole (E2) character between most bound negative ion levels. Such "forbidden" transitions have very recently been reported between fine structure levels of Ir^- and Pt^-, although the lack of a confirmation via a two-photon Raman transition left the M1 interpretation somewhat open [5]. In this paper we present a case study where a combination of one-, two-, and three-photon detachment experiments is utilized to completely and accurately determine all bound terms and fine structure levels of the antimony negative ion. The results fully confirm the potential of forbidden transitions in optical studies of negative ions [5]. Also, a single-color 2 + 1 photon detachment scheme is demonstrated for the first time, suggesting prospects for the study of some weakly bound excited states in other systems. In addition, we present RCI calculations of fine structure and term splittings and of hyperfine structure constants. Finally, these constants are used to simulate the observed thresholds and M1 resonance peak profiles.

The experimental setup is described in detail elsewhere [4–6]. Nanosecond pulses in the 0.7–1.0 μm range are generated using a dye laser which is pumped by the second harmonic of a 10 Hz Q-switched Nd:YAG laser. Stimulated Raman scattering in a single pass high pressure hydrogen cell is employed to convert the dye laser output into tunable infrared radiation via first and second Stokes generation, with a measured Raman shift of 4155.20(2) cm^{-1}. Infrared pulse energies range from 10 mJ at 1 μm to 0.1 mJ at 5 μm. A 15 keV Sb^- beam is extracted from a Cs sputter ion source, magnetic field analyzed, and further charge state analyzed in an ultrahigh vacuum chamber and then crossed perpendicularly with a collimated or focused infrared laser beam (for single photon or multiphoton detachment, respectively). The photodetached neutral atoms impinge on a discrete dynode electron multiplier for analog data collection.

A schematic energy level diagram of the negative ion of antimony is shown in Fig. 1. To our knowledge, only two photodetachment experiments with this system have been reported previously. Feldmann *et al.* [7] used a conventional light source and obtained a $^3P_2$ binding energy of 8630(400) cm^{-1} and a $^3P_2 - {}^3P_{1,0}$ fine structure splitting of 2740(600) cm^{-1}. The $J = 1, 0$ levels remained unresolved. The $J = 2 - 1$ and $J = 2 - 0$ fine structure and $^3P_2 - {}^1D_2$ term splittings have been predicted to be 2700(500), 3000(500), and ~7600 cm^{-1} on the basis of isoelectronic extrapolation [8,9]. Polak *et al.* [10] derived an electron affinity of 8436(40) cm^{-1} from a laser photodetached electron spectrum and reported that no evidence of hot bands was observed.

The photodetachment spectrum of Sb^- in the vicinity of the $Sb^-(^3P_2) \rightarrow Sb(^4S_{3/2})$ threshold is shown in Fig. 2. Wigner's threshold law which applies to the

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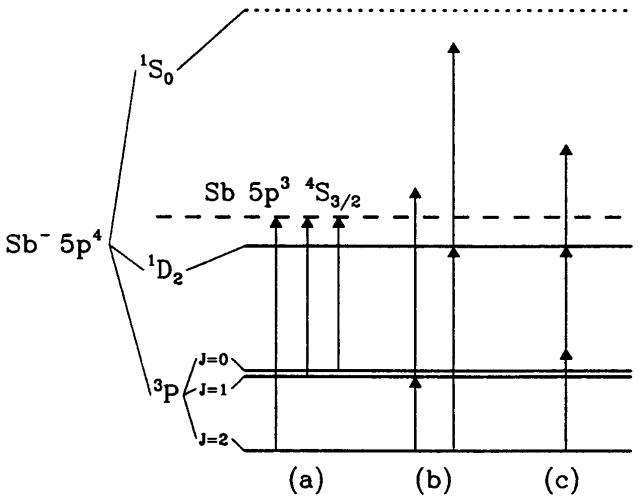

FIG. 1. Schematic energy level diagram of Sb^-. Arrows indicate different photodetachment schemes: (a) single photon detachment thresholds; (b) two-photon detachment via single photon M1 resonances; (c) three-photon detachment via two-photon E1 resonance.

photodetachment of negative ions predicts the cross section to be proportional to $\varepsilon^{\ell+1/2}$ where ε is the energy of the detached electron and ℓ its angular momentum. Detachment of a bound p electron therefore exhibits an s-wave threshold which has been fitted to the experimental data (dashed line in Fig. 2). From this fit, a $Sb^-(^3P_2)$ binding energy of 8447.83(15) cm^{-1} is obtained. (Uncertainties will always include possible systematic errors due to laser calibration and Doppler shifts.) This result is in good agreement with the previous measurements, but exhibits a nearly 300-fold increase in accuracy. The foot right at the onset of the threshold in Fig. 2 indicates line broadening effects due to hyperfine structure (see below) in addition to the effects of laser bandwidth and Doppler broadening, the latter two of which, if combined, are typically less than 0.2 cm^{-1}. Two more, although significantly weaker, thresholds are found at photon energies of 5763.3(3) and 5647.0(5) cm^{-1} which results in fine structure splittings of 2684.5(4) and 2800.8(6) cm^{-1} between the $^3P_2$ ground level and the two upper levels of the ^3P term. The most likely order of the ^3P_J levels is certainly 2-1-0 but the large uncertainties of isoelectronic extrapolations leave a small probability for a 2-0-1 order as it is found throughout the isoelectronic sequence. To be sure, a 1 + 1 two-color photodetachment experiment is conducted which employs second Stokes radiation around 3.6 μm for the resonant transition and first Stokes radiation for the subsequent detachment. Only one resonance is found at 2684.37(15) cm^{-1} as shown in Fig. 3 and must be assigned to a transition between $^3P_2$ and $^3P_1$, confirming a 2-1-0 level order. This assignment is based on estimated transition probabilities of 0.4 s^{-1}(M1) and 0.9×10^{-3} s^{-1} (E2) for $J = 1 \rightarrow 2$ and 2×10^{-3} s^{-1} (E2) for $J = 0 \rightarrow 2$ which are derived from probabilities for forbidden transitions in the $5p^k$ configurations, calculated by Biémont *et al.* [11]. According to that, a $J = 2 \rightarrow 0$ electric quadrupole transition would be about 200 times weaker than the dominantly magnetic dipole $J = 2 \rightarrow 1$ resonance, too weak to be observed under the given experimental conditions.

In order to locate the previously unobserved but possibly bound $^1D_2$ term, the single-color two-photon detachment spectrum of $Sb^-(^3P_2)$ was recorded. Isoelectronic $^1D_2 \rightarrow {}^3P_2$ transition probabilities of 1.1 s^{-1} (M1) and 3×10^{-2} s^{-1} (E2) (based on Ref. [11]) suggest that a 1 + 1 resonance should be of M1 character and observable under the given experimental conditions. Figure 4 shows this resonance which was found at a photon energy of 7392.55(15) cm^{-1} giving a $^1D_2$ binding energy

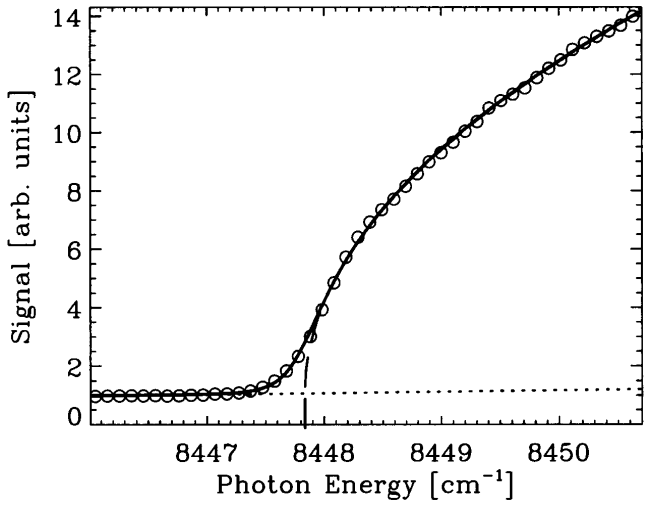

FIG. 2. Measured $Sb^-(^3P_2) \rightarrow Sb(^4S_{3/2})$ photodetachment threshold. Wigner s-wave fits with and without the inclusion of line broadening effects are indicated by the solid and dashed line, respectively.

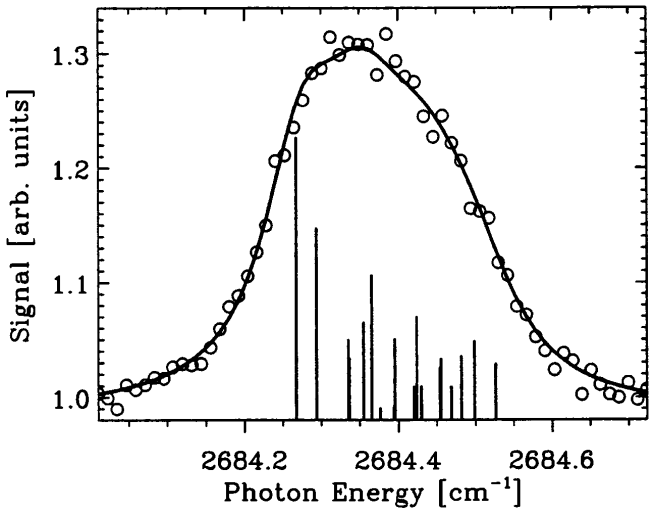

FIG. 3. $^3P_2 \rightarrow {}^3P_1$ M1 resonance in the two-photon detachment yield. The solid line represents the simulated resonance profile (see text), and the vertical lines indicate positions and relative strengths of individual hyperfine components.

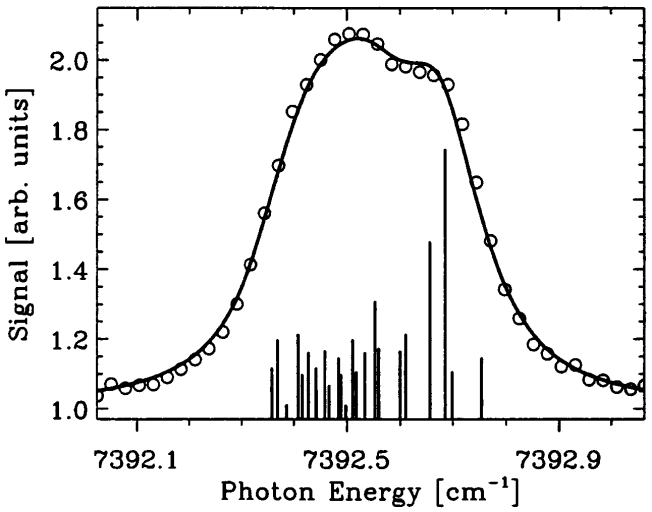

FIG. 4. $^3P_2 \rightarrow {}^1D_2$ M1 resonance in the two-photon detachment yield. The solid line represents the simulated resonance profile (see text), and the vertical lines indicate positions and relative strengths of individual hyperfine components.

of 1055.3(2) cm^{-1}. In order to check the level parity, the $^3P_2 \rightarrow {}^1D_2$ transition was also driven via an electric dipole allowed two-photon absorption. As the $^1D_2$ binding energy is less than half the $^3P_2 - {}^1D_2$ splitting energy, the transition could be observed as a 2 + 1 resonance in the single-color three-photon detachment spectrum of $Sb^-(^3P_2)$. The signal-to-background ratio of this resonance was significantly improved by retaining a fraction of the first Stokes radiation in the infrared pulse. In doing so, the probability for absorption of the third and detaching photon was substantially increased and only a small single photon detachment background from the upper ^3P_J levels was introduced. A photon energy of 3696.35(15) cm^{-1} gives a splitting energy of 7392.7(3) cm^{-1} which agrees well with the value obtained from the 1 + 1 M1 resonance.

All three resonances observed in Sb^- exhibit a line broadening that cannot be explained on the basis of laser bandwidth and Doppler effects alone. A comparison with the equivalent transitions in isoelectronic Te and I^+ [12] and transitions between levels of the $5p^3$ configuration in Sb [13] indicates that Sb^- hyperfine structure could give rise to a broadening of a few tenths of wave numbers. The hyperfine structure of numerous neutral and positively charged systems has been studied in the optical regime, but studies of this kind do not exist for negative ions. Therefore, the measured 1 + 1 M1 resonance peak profiles have been modeled on the basis of calculated hyperfine structure A and B constants (see below). The energy E_F of a hyperfine sublevel F belonging to a fine structure level J with average energy E_J is given by

$$E_F = E_J + A\frac{C}{2} + B\frac{3C(C+1) - 4IJ(I+1)(J+1)}{8IJ(2I-1)(2J-1)},$$

where $C = F(F+1) - J(J+1) - I(I+1)$. The relative intensity of a hyperfine component ($F \rightarrow F'$) of a fine structure transition ($\alpha J \rightarrow \alpha' J'$) can be expressed as

$$S_{FF'} \propto (2F+1)(2F'+1)\begin{Bmatrix} I & J & F \\ j & F' & J' \end{Bmatrix}^2,$$

where $j = 1$ for dipole transitions (or $j = 1/2, 3/2$ for s-wave thresholds; see below). In the case of Sb^- the spectral profile of a single component could not be measured directly but it is inferred to be mainly Lorentzian with a width of 0.16(2) cm^{-1} (FWHM) based on previously measured M1 resonances [5]. The best overlap of measured and calculated profiles is found by performing a least square fit using $\Delta E = E_{J'} - E_J$ and the peak height as fitting parameters. Unfortunately, the measured profiles do not exhibit enough structure for hyperfine A and B constants to be included as parameters in the fit which would result in experimental values for these constants. Instead, the calculated values are used. Figures 3 and 4 show the fitted data including line spectra which indicate the individual hyperfine components. The transition energies ΔE obtained from the fit are those given in the preceding paragraphs. The situation was complicated due to the fact that the antimony used in the sputter cathode contained both isotopes ^{121}Sb and ^{123}Sb in their natural abundances of 57% and 43%. As a result, the two M1 resonances were composed of 18 and 26 hyperfine components, respectively. Nevertheless, the good agreement between measured and calculated line profiles is a convincing indication of hyperfine structure in the bound levels of Sb^-. The interpretation is consistent with the fact that the previously observed bound-bound transitions in Ir^- and Pt^- [5] and high resolution threshold spectra of other negative ions [1] did not exhibit additional line broadening as the corresponding nuclei have zero spin or only small magnetic dipole and electric quadrupole moments or the electronic angular momentum J is zero.

As mentioned above, the $Sb^-(^3P_2) \rightarrow Sb(^4S_{3/2})$ threshold appears broadened as well. It is composed of several closely spaced thresholds due to the hyperfine structure in both the neutral atom [13] and negative ion states. The threshold was modeled using the above equations, convoluted with the line shape function, and then fitted to the data (solid line in Fig. 2). This resulted in an average $Sb^-(^3P_2)$ binding energy of 8447.79(15) cm^{-1}, $^{121}Sb^-(^3P_2, F = 1/2)$ and $^{123}Sb^-(^3P_2, F = 3/2)$ binding energies of 8447.87(15) and 8447.85(15) cm^{-1} (relative to the lowest hyperfine level of the respective atom), and finally an isotopically averaged electron affinity of antimony of 8447.86(15) cm^{-1}.

Since the experimental conditions did not allow for a discrimination between the two isotopes of Sb, the possibility of isotope shifts should be considered. Calculated values for the normal mass shifts of the observed M1 transitions are 6 MHz for $^3P_2 \rightarrow {}^3P_1$ and 15 MHz for $^3P_2 \rightarrow {}^1D_2$ [14]. Buchholz *et al.* [15] measured isotope shifts in transitions between the $5s^25p^3$ and $5s^25p^26s$

configurations of neutral antimony. The residual isotope shifts in these transitions are smaller than 300 MHz and indicate that residual shifts in transitions between the ^2P and ^2D terms of the $5p^3$ configuration would only be of the order of 30 MHz. We therefore conclude that isotope shifts in the $^3P_2 \rightarrow {}^3P_1$ and $^3P_2 \rightarrow {}^1D_2$ transitions of Sb^- should be no larger than 100 MHz (or 0.003 cm^{-1}), i.e., 2 orders of magnitude smaller than the calculated hyperfine splittings.

Relativistic configuration interaction (RCI) calculations were carried out by first obtaining a Dirac-Fock wave function for $5p^4$ using the program of Desclaux [16]. The Dirac-Coulomb Hamiltonian was used during the variation, and Breit effects added perturbatively. The Dirac-Fock solution was then correlated, using our RCI program [17], by including single and double excitations from the $5s$ and $5p$ subshells, and single excitations from the $4d$ subshell. To substantially reduce the amount of excitation needed, all energies were referenced to the negative ion ground state. For energy differences the most important excitations were $5p \rightarrow vf$, $5s \rightarrow vd$, and $4d \rightarrow vg$, where the virtual (unoccupied) subshells are represented by relativistic screened hydrogenic functions. Further details of the methodology may be found elsewhere [18,19]. The calculations predict the $^3P_1$, $^3P_0$, and $^1D_2$ levels to lie 2516, 2831, and 7628 cm^{-1} above the $^3P_2$ ground level, respectively. These values are in good agreement with the experimentally determined energy splittings given above. In addition, RCI results indicate the $^1S_0$ level to lie $\approx$16 700 cm^{-1} above $^3P_2$, i.e., to be unbound by $\approx$8350 cm^{-1}. Using the RCI wave functions, hyperfine structure constants were calculated. The magnetic dipole A constants are -292, 489, and 1264 MHz for the $^3P_1$, $^3P_2$, and $^1D_2$ levels of $^{121}Sb^-$, respectively, and -158, 265, and 684 MHz for the corresponding levels of $^{123}Sb^-$. For these three levels calculated B/Q values are -321, 647, and -1423 MHz/b from which the electric quadrupole B constants are obtained using $Q_{121} = -0.36$ b and $Q_{123} = -0.49$ b [15]. Results for matrix elements of hyperfine structure operators can be found in Ref. [20].

In summary, infrared laser experiments have provided accurate binding energies for all four bound levels of Sb^-. The $^3P_1$, $^3P_0$, and $^1D_2$ levels were observed for the first time. Level splittings obtained from RCI calculations support the experimental results. The studies have clearly confirmed that magnetic dipole transitions in negative ions can be observed under typical experimental conditions with pulsed laser sources and keV ion beams. Resonance peak profiles have been successfully modeled on the basis of calculated hyperfine structure constants, indicating the potential of multiphoton spectroscopy in the experimental determination of negative ion hyperfine structure. In addition, a single color two-photon (bound-bound) transition was demonstrated for the first time in negative ions. In the study of other negative ion systems this transition scheme may provide a probe for weakly bound excited states which often cannot be addressed otherwise. To conclude, the combination of single and multiphoton techniques illustrated in this work provides a complete approach to the study of bound levels of atomic negative ions.

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