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Electron-impact excitations of the autoionizing states of bismuth

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Abstract

Electron-impact excitation from the ground state of bismuth has been studied with electron energy-loss spectra. We have identified 14 autoionized states in the region up to 13.5 eV. Three states at 7.34, 9.97 and 11.2 eV have been recorded for the first time, they have not been observed previously either in photoabsorption spectroscopy or in arc spectra. The present energy level values are compared with the limited number of available data.

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Keywords: Bismuth atom; Autoionization; Electron energy-loss spectroscopy

1. Introduction

Bismuth is an atom that has been driving a considerable interest recently, from investigations of electron collisional cross-sections [1], determination of transition probabilities of astrophysical interest [2] to studies of Bi nanowires and their potential applications in the nanotechnology industry [3,4]. There are several measurements of absorption spectra at different wavelength ranges, the earlier results were summarized by Moore [5] and later reported by Mathews et al. [6]. Theoretical studies of electron interactions with bismuth started with the investigation of exchange effects at low impact energies [7] and were extended to the determination of differential cross-sections [8,9], as well as the recent calculations of spin polarization of elastically scattered electrons [1]. Experimental studies comprise measurements of differential cross-sections (DCS) for elastic scattering and the excitation of a limited number of states [10], at the single incident electron energy of 40 eV, and the spin polarization of elastically scattered electrons by heavy atoms including bismuth [11]. Autoionizing lines in bismuth had been also studied in an arc spectrum [12,13].

Autoionization has a significant influence on the ionization rate when autoionizing elements are present in a plasma medium. Scattered electron intensity observation is a powerful method to investigate excitation of atomic autoionizing states, in two ways: by direct angular distribution measurement and by recording the energy-loss spectra. In the present study, we have employed an electron spectrometer in a crossed-beam arrangement to record energy-loss spectra at electron-impact energies of 10, 20, 40, 60, 80 and 100 eV. If a target atom is in the ground state, lines observed in electron energy-loss spectra are directly attributed to their excited states, without any confusion due to decay channels in autoionization.

The contribution of autoionization to the total ionization cross-sections has been examined in detail by Kim and Stone, in particular for IIIA group atoms of the Periodic Table (boron, aluminum, gallium, indium) [14] and IVA group atoms [15]. They concluded that autoionization contributes about as much to the total ionization of IIIA group atoms as does direct ionization. The major contribution arises from the first set of autoionizing levels. They also considered indirect ionization processes such as excitation–autoionization and found the conditions when these core-excited states contributed significantly to autoionization (Sec. IIIE in Ref. [14]).

2. Experimental

The apparatus is a conventional crossed-beam electron spectrometer described elsewhere [16,17]. In brief, hemispherical energy selectors in both the monochromator and analyzer are

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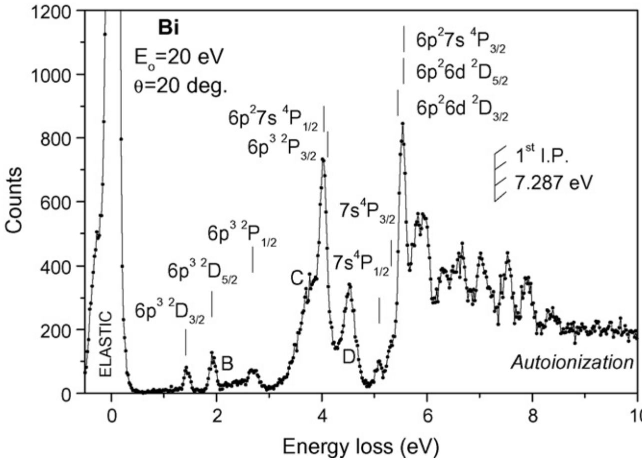

Fig. 1. Electron energy-loss spectrum of bismuth at 20 eV impact energy and a scattering angle of 20°.

made of molybdenum, while all cylindrical lenses are made of gold plated OFHC copper (see a schematic overview of the electron spectrometer in Fig. 1 at Ref. [17]). The operating conditions are summarized in Table 1.

The energy scale was calibrated against the 3s3p $^1P_1$ excitation threshold of Mg at 4.346 eV. Using a significantly improved energy resolution (50 meV), we did not find any shift in the energy scale due to the contact potential difference between the thoriated tungsten filament and the collision chamber. The position of the zero scattering angle was determined before each angular distribution measurement by checking the symmetry of the scattered electron signal at positive and negative angles, with respect to the un-scattered electron beam.

To produce an effusive gas-beam from bismuth chucks, we used a resistively heated oven made of stainless steel. Monitoring of the temperature at the bottom and at the top of the crucible was necessary in order to provide stable conditions for the target beam. A higher temperature at the top end protected the nozzle from clogging, while the constant temperature at the bottom provided the right conditions for the atomic gas flow. Water cooling of the oven shield protected the channel electron multiplier from a rise in temperature during long-term measurements. The presence of bismuth dimers could not be avoided and the molecular features attributed to Bi_2 have been recorded in each energy-loss spectrum. Both atomic and molecular transitions were also observed by Williams et al. [10].

Table 1
The experimental conditions of our electron spectrometer

Parameters	Condition
Impact energy range (eV)	10–100
Energy resolution (meV)	100–150
Uncertainty in energy scale (meV)	300
Angular range of the spectrometer	−30 to 150
Angular resolution (°)	1.5
Uncertainty in angular scale (°)	0.5
Oven temperature (K)	1000
Metal–vapour pressure (Pa)	10
Oven nozzle aspect ratio ($\gamma = d/L$)	0.075
Primary electron current (nA)	10–50
Residual magnetic field in the interaction region (double μ—metal shield) (μT)	<0.1
Background pressure (mPa)	<5

3. Results and discussion

We have recorded energy-loss spectra of bismuth atom at electron-impact energies of 10, 20, 40, 60, 80 and 100 eV. The electron excitation of the first excited states is presented in an electron energy-loss spectrum at 20 eV impact energy and a scattering angle of 20° as shown in Fig. 1. The autoionization region covered by these spectra is from the first ionization limit (7.287 eV) up to 13.5 eV, and it is broad enough to include the fifth ionization limit (12.763 eV). An energy-loss spectrum of the autoionization region at 100 eV and 6° is presented in Fig. 2.

The ground state of bismuth is of quartet S symmetry with configuration [Hg]6p^3 $^4S^0_{3/2}$. Single photon absorption spectra show dipole-allowed transitions from the ground state to even-parity levels with $\Delta J = 0, \pm 1$. The first excited states are labeled as the 6p^3 $^2D_{3/2,5/2}$ (energy losses of 1.416 and 1.914 eV) and 6p^3 $^2P_{1/2,3/2}$ (energy losses of 2.685 and 4.111 eV) of odd parity [5]. The excited states belong to different Rydberg series that converge to the 6p^2 $^3P_{0,1,2}$ ground terms of Bi^+. Levels of different Rydberg series with the same parity and J value interact with one another. Below the 6p^2 $^3P_0$ first ionization limit of bismuth, Moore [5] listed 33 even-parity levels, which were assigned mainly to the series 6p^{2}ns ^{2,4}P or 6p^{2}nd ^{2}D. The first ionization level has been improved in accuracy to the value of 58761.68 cm^{-1} by Bühler et al. [18] over the previously tabulated value. The 6p^2 $^3P_1$ ionization limit has been determined at 8.938 eV and the 6p^2 $^3P_2$ ionization limit being 9.398 eV. Mathews et al. [6] have investigated photoabsorption spectra in the region from 202.2 to 130.7 nm (6.132–9.486 eV). They interpreted the transitions below the 6p^2 $^3P_1$ ionization limit by using two-limit multichannel quantum defect theory. They found four Rydberg series (labeled A–D) in the region between the first ($^3P_0$) and the second ionization limits ($^3P_1$) and two prominent series (labeled X, Y) and one weak, diffuse series (labeled Z) between the second and the third ($^3P_2$) ionization

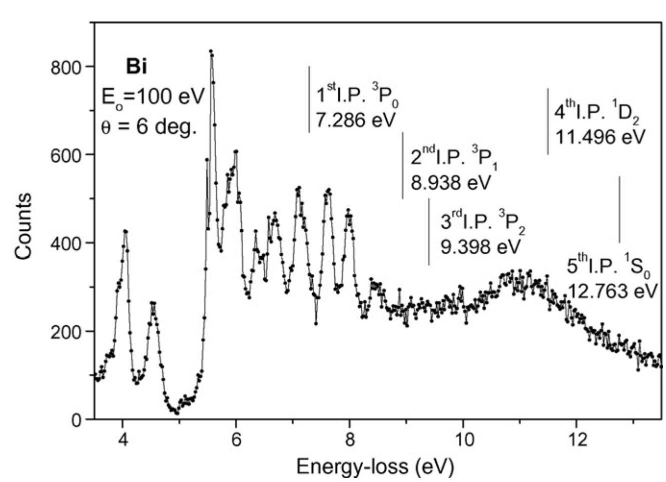

Fig. 2. Electron energy-loss spectrum of bismuth at 100 eV impact energy and a scattering angle of 6°. The first five ionization limits are indicated.

Table 2
Autoionizing states of bismuth recorded in electron energy-loss spectra

Energy loss (eV)	Clearman [12] (eV)	Assous [13] (eV)	Mathews et al. [6] (eV)	Moore [5] (eV)	Remark
7.34	–	–	–	–	Observed for the first time; shoulder
7.55	7.537 $6p^2(^3P_1)8s$ $J=3/2$	7.539 $6p^2(^3P_1)8s$ $^4P_{3/2}$	7.540 $J=3/2$ or 5/2	7.540 $6p^2(^3P_1)8s$ $J=3/2$	
7.62	7.621 $6p^2(^3P_2)6d$	7.664 $6p^2(^3P_2)6d$ $^4F_{3/2}$	7.579	7.624 $6p^2(^3P_2)6d$ $J=1/2$	
7.77	7.776 $6p^2(^3P_2)6d$	7.777 $6p^2(^3P_2)6d$ $^4D_{3/2}$	–	7.779 $6p^2(^3P_2)6d$ $J=3/2$	
7.89	7.914 $6p^2(^3P_1)8s$ $J=5/2$	–	7.917 series B $J=1/2$ or 3/2	7.902 $6p^2(^3P_1)8p$ $J=1/2$	Shoulder
7.98	7.966	8.051 $6p^2(^3P_1)7d$	7.969 $J=1/2$ or 3/2	7.969 $6p^2(^3P_1)7d$ $J=3/2$	
8.16	–	–	8.135	8.135 $6p^2(^3P_1)9s$ $^2P_{1/2}$	
8.27	8.318 $6p^2(^1D_2)7s$	–	–	8.248 $6p^2(^3P_1)9p$ $J=1/2$	
8.43	8.434 $6p^2(^3P_2)7d$	–	8.436	8.410 $6p^2(^3P_1)10s$ $^4P_{3/2}$	
8.61	–	–	8.634 series B	8.570 $6p^2(^3P_1)9s$ $^2P_{3/2}$	
8.88	–	–	8.875 series B or D	8.865 $6p^2(^3P_1)10s$ $^2P_{3/2}$	
9.09	9.094 $6p^2(^3P_2)10p$	–	9.097 series X	9.097 $6p^2(^3P_1)10d$ $J=1/2$	
9.27	–	–	9.264 series Y	–	
9.97	–	–	–	–	Observed for the first time
11.2	–	–	–	–	Observed for the first time; broad feature about 0.9 eV

Eleven states are identified between the first (7.286 eV) and second (8.938 eV) ionization limits, two states between the second and the third (9.398 eV) and two between the third and the fourth (11.496 eV). The assignments of the autoionizing states by different authors are indicated.

limits. The fourth and the fifth ionization limits correspond to the core-excited states $^1D_2$ (at 11.496 eV) and $^1S_0$ (at 12.763 eV), respectively.

In Fig. 1, features that correspond to the excited atomic states are labeled according to the assignment in Moore's tables [5], while dimer states are labeled according to Huber and Herzberg [19]. We could identify Bi_2 transitions at 2.20 eV (B), 3.97 eV (C) and 4.52 eV (D). Due to the generally lower resolution in electron spectroscopy, it was not possible to observe any new dipole-allowed excited levels in this energy domain that had not previously been observed in photoabsorption spectra. The observation of dipole-forbidden levels below the first ionization limit was not successful due to very dense spectrum of the Bi atom and many overlapping states. Also, the scattered electron signal diminishes significantly as the analyzer is moved towards higher scattering angles where the dipole-forbidden transitions are expected to show up more clearly.

In Fig. 2 several autoionizing states are identified and they are listed in Table 2. The first state after the ionization level has been observed as a shoulder at the energy loss of 7.34 eV. There is no evidence of this state in photoabsorption spectra. The strong state at 7.77 eV is well known from both photoabsorption and arc spectra, and it has been assigned as the $6p^2(^3P_2)6d$ state. The states at 7.89 and 8.88 eV have been attributed to the Rydberg series B by Mathews et al. [6]. Another intense state at 7.98 eV has been assigned as the $6p^2(^3P_1)7d$ state. The assignment of several weaker states observed at energies of 8.16, 8.27, 8.43 and 8.61 eV is rather ambiguous and it has been done according the Moore's tables [5].

Two states at 9.09 and 9.27 eV have been identified as autoionizing states between the second and third ionization limits. The first state has been classified as a member of Rydberg series X, while the second is seen as a member of the Y series by Mathews et al. [6]. The two states at 9.97 and 11.2 eV, that have not been observed previously in either photoabsorption or in arc spectra, lie in the energy-loss region between the third and fourth ionization limits of bismuth. The feature at 11.2 eV is very broad (about 0.9 eV half width of full maximum).

4. Conclusions

In summary, we have obtained electron energy-loss spectra of bismuth and we have identified 14 autoionized states in the energy-loss region up to 13.5 eV. Three states at 7.34, 9.97 and 11.2 eV have been recorded for the first time, they have not been observed previously in either photoabsorption spectroscopy or in arc spectra. Apart from measurements at 40 eV incident electron energy and below the ionization limit, no other experimental data of electron energy loss has been available until now. Providing more experimental electron scattering data is crucial for a better understanding of the bismuth atom and, consequently, differences and similarities within the VB group of the Periodic System of Elements.

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