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Theoretical and experimental study of the electronic states and spectra of KBi and KSb

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ABSTRACT

Gas phase emission spectra of the hitherto unknown free radicals KBi and KSb were measured in the NIR range with a Fourier-transform spectrometer. The emissions were observed from a fast-flow system in which bismuth or antimony vapor in argon carrier gas was passed through a microwave discharge and mixed with potassium vapor in an observation tube. For KBi, two systems of blue-degraded bands observed in the range 5800–7700 cm^{-1} are assigned to the transitions $A^3\Pi$ $(A_20^+) \rightarrow X^3\Sigma^-(X_10^+, X_21)$. Nine bands of the $A_20^+ \rightarrow X_10^+$ and three bands of the $A_20^+ \rightarrow X_21$ system were measured at high spectral resolution and rotationally analysed. The rotational and vibrational analyses yielded the spectroscopic parameters of the X_10^+, X_21, and A_20^+ states. For KSb, in the range of the sensitive Ge detector, only one sequence of bands was measured near 6880 cm^{-1}. By analogy with the previously observed spectra of NaSb and NaAs these bands were identified to be the $\Delta v = 0$ sequence of the a2 $\rightarrow X_21$ transition of KSb. Some very weak bands observed at low resolution in the range 3800–5200 cm^{-1} are assigned to the transitions $A^3\Pi$ $(A_21) \rightarrow X^3\Sigma^-(X_10^+, X_21)$.

To aid in the analysis of the experimental data, a series of relativistic configuration interaction calculations has been carried out to obtain potential energy curves for the low-lying states of KBi and KSb, vibrational constants, equilibrium internuclear distances, and also electric dipole transition moments connecting the states.

1. Introduction

Due to their equal outer electronic configurations, the mono-hydrides and the mono-alkali compounds of the group Va elements (NH, PH, . . ., BiH and LiN, NaN, . . ., CsBi) exhibit the same Λ–S electronic states. However, due to different bonding (covalent *vs.* ionic) the relative energy positions of the states are substantially different in the two groups. Light molecules of these groups coupled according to Hund's case (a) or (b) exhibit $X^3\Sigma^-$ ground states and low-lying $a^1\Delta$ and $b^1\Sigma^+$ excited states all arising from the same $\ldots\sigma^2\pi^2$ electron configuration. For the hydrides, all other bound states arising from the $\ldots\sigma\pi^3$ and $\ldots\sigma\pi^2\sigma^*$ configurations lie at much higher energies (above 25,000 cm^{-1}). For the alkali compounds, however, some of these states come down in energy. In particular, the $A^3\Pi(\ldots\sigma\pi^3)$ state here lies in the same energy range or even lower than the $a^1\Delta$ state. In heavy-atom containing molecules coupled according to Hund's case (c), spin-spin and spin-orbit (SO) coupling causes the $X^3\Sigma^-$ ground state to split into two Ω-components X_10^+ and X_21, and the excited Λ–S states $A^3\Pi$, $a^1\Delta$, $b^1\Sigma^+$ and $c^1\Pi$ of the alkali compounds give rise to a number of low-lying Ω states with $\Omega = 0^+, 0^-, 1$ and 2 which all can undergo allowed near-infrared transitions to one or both ground state components.

In previous studies of the alkali-group Va compounds we started with the alkali-bismuth molecules NaBi [1] and LiBi [2] which, due to large SO splitting, were expected to show well separated electronic states and transitions. However, *ab initio* relativistic CI calculations of the electronic states of the molecules showed that for these Bi compounds only two low-lying excited Ω states, A_12 and A_20^+, have bound potential energy curves. In the wavenumber range accessible with our Ge (5900–12,000 cm^{-1}) and InSb (3200–6000 cm^{-1}) detectors, only two band systems were observed. They were assigned to the $A_20^+ \rightarrow X_10^+$ and $A_20^+ \rightarrow X_21$ transitions.

Subsequent studies of the spectra of NaSb [3] and NaAs [4] showed that in these lighter molecules all seven Ω states arising from the $A^3\Pi$, $a^1\Delta$, $b^1\Sigma^+$ and $c^1\Pi$ states have bound potential energy curves. For both molecules seven transitions from the

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lowest-lying states A_12, A_21, A_30^+, A_40^- and $a2$ were observed and analysed.

In the present paper we report on relativistic CI calculations and Fourier-transform emission studies of the near-infrared spectra of the hitherto unknown molecules KBi and KSb. As expected, the observed spectra were found to be quite similar to those of the previously studied NaBi [1] and NaSb [3] molecules.

2. Experimental details

As in previous work [1–4], the source of the emission spectra was a fast-flow system made of Pyrex glass and quartz tubes in which the KBi or KSb molecules were excited in the reaction of potassium vapor (K_x) with a microwave-discharged Bi_x/Ar or Sb_x/Ar mixture. The potassium vapor (K_x) in Ar carrier gas was generated by flowing Ar over a few grams of potassium metal in a ceramic boat heated to about 400 °C in a quartz tube. More details of the experimental set-up and the spectroscopic equipment are given in our recent work on LiBi [2].

3. Experimental results and analyses

3.1. KBi

Fig. 1 shows two sections of a survey spectrum of the chemiluminescence emitted from the reaction of MW-discharged Bi_x/Ar with K_x/Ar recorded at a resolution of 0.5 cm^{-1}. Two systems of blue-degraded bands are observed in the ranges 6500–7700 cm^{-1} and 5800–6400 cm^{-1}. Both transitions consist of several sequences of bands with sharp heads in the P branches and thus look quite similar to the band systems observed for NaBi [1] and LiBi [2]. Again the relative intensities of the sequences suggest that the electronic states involved in the transitions have nearly parallel potential energy curves. Assuming that the strongest sequences are those with $\Delta v = 0$, the bands were assigned and vibrational analyses of the band heads were performed which readily showed that both systems originate from the same upper state. High-resolution spectra (0.018 cm^{-1}) showed that the bands of the 7000 cm^{-1} system consist of P and R branches only whereas those of the 6020 cm^{-1} system contain P, Q, and R branches. These results suggest that the systems are due to transitions from an $\Omega = 0^+$ upper state to the X_10^+ and X_21 components of the $X^3\Sigma^-$ ground state of KBi. In the light of the theoretical and experimental results for NaBi [1] and LiBi [2] and the theoretical calculations reported below, the band systems, therefore, are assigned to the $A_20^+ \rightarrow X_10^+$ and $A_20^+ \rightarrow X_21$ transitions of KBi.

Nine bands of the $A_20^+ \rightarrow X_10^+$ and three bands of the $A_20^+ \rightarrow X_21$ system were rotationally analysed. The formalism used in the analyses has been described in detail in Ref. [2]. Again identification and fitting of the rotational lines was greatly facilitated by using "*PGOPHER, a program for simulating and fitting rotational structure*", written by C.M. Western from the University of Bristol [5]. The PGOPHER input files of all fitted bands, which contain the measured vacuum wavenumbers of the analysed rotational lines, together with data point tables of the spectra for overlays in the simulated spectra are available from the "*Depository of supplementary material*" of the Journal. The parameters obtained from the fits are given in Tables 1 and 2. Figs. 2 and 3 show sections of the high-resolution spectra of the 0–0 bands together with simulated spectra calculated with the parameters given in Tables 1 and 2 for a rotational temperature of 320 K.

Table 3 shows the wavenumbers and observed-calculated differences of the band origins used for vibrational analyses of the two systems. In the case of the $A_20^+ \rightarrow X_10^+$ system, only the accurate band origins of the nine bands which were rotationally analysed were used in the fit. For the $A_20^+ \rightarrow X_21$ system where three such accurate band origins only were known, additional approximate band origins were obtained by correcting the wavenumbers of the P-branch heads read from medium-resolution spectra by the wavenumber differences between the heads and the origins ν_H-$\nu_0 = -(B'_v + B''_v)^2/4(B'_v - B''_v)$ [6] obtained from the rotational analyses of the bands. Here it was assumed that the ν_H-ν_0 data are approximately constant for the bands of a sequence. So for bands of the $\Delta v = 0$ and $\Delta v = +1$ sequences corrections of +0.98 cm^{-1} and +1.13 cm^{-1} obtained from the 0–0 and 1–0 bands were used. The value +1.28 cm^{-1} used for the bands of the $\Delta v = +2$ sequence was obtained by extrapolation of these two values. In the fits, the accurate wavenumbers of the bands which were rotationally analysed were given five times higher weights than the other data. The vibrational parameters and equilibrium rotational parameters are given in Table 4.

Since the $A_20^+ \rightarrow X_10^+$ and $A_20^+ \rightarrow X_21$ transitions originate from the same upper state, the relative intensities of bands with the same Frank-Condon (FC) factor yields the ratio of the transition probabilities $A_{A2\text{-}X1}/A_{A2\text{-}X2}$. Assuming then that the FC-factors of the 0–0 bands are approximately the same and correcting for the wavenumber dependence of the sensitivity of the detection system, from the integrated intensities of these bands (Figs. 2 and 3) we obtain $A_{A2\text{-}X1}/A_{A2\text{-}X2} = 1.6 \pm 0.5$.

3.2. KSb

Due to a break-down of our FT spectrometer, only a few low-resolution spectra of KSb could be measured. Different from all previously studied alkali-group V molecules, in the sensitivity range of the Ge detector the spectrum of KSb contains only a single sequence of narrow molecular bands near 6890 cm^{-1} (Fig. 4a). By analogy with the spectra of NaSb [3] and NaAs [4] these bands are assigned to be the $\Delta v = 0$ bands of the $a2 \rightarrow X_21$ transition of KSb. The $\Delta v = +1$ and $\Delta v = -1$ sequences expected to show up at about 150 cm^{-1} higher and lower wavenumbers are at least by a factor of 30 weaker than the $\Delta v = 0$ bands (Fig. 4b) showing that the two states involved must have potential energy curves with quite similar shapes and r_e values.

In the sensitivity range of our InSb detector (3200–5800 cm^{-1}), only eight weak bands were observed between 4000 and 5000 cm^{-1} (Fig. 5). In the light of the theoretical results (see below) these bands are assigned to the transitions $A_21 \rightarrow X_10^+$ and $A_21 \rightarrow X_21$ as indicated in the figure. By comparison with the corresponding data of NaSb [3] and KBi (Table 4) we estimate the anharmonicity constants of KSb in the X_1, X_2 and A_2 states to be $\omega_e x_e = 0.4 \pm 0.1$ cm^{-1}. Fixing the $\omega_e x_e$ parameters of X_1, X_2 and A_2 to this value, a joint fit of the eight band heads ($\cong \upsilon_0$ values, Table 6) yielded the ω_e and T_e data of X_1, X_2 and A_2 given in Table 7.

Fixing the ω_e and $\omega_e x_e$ constants of X_2, the band heads ($\cong \upsilon_0$ values) of the $a2 \rightarrow X_21$ bands (Table 6) were fitted to get the vibrational constants and the T_e value of the $a2$ state (Table 7).

In order to support the assignments of the bands, we have simulated the 0–0 bands of the three transitions $A_21 \rightarrow X_10^+$, $A_21 \rightarrow X_21$ and $a2 \rightarrow X_21$ and compared the band contours with the experimental band shapes. The centrifugal distortion constants D and the Ω-doubling constants in the X_21 and A_21 states are expected to be very small, in the order of 10^{-8} and 10^{-4} cm^{-1}, respectively (Kratzer value $D \cong 7 \times 10^{-9}$ cm^{-1}). Therefore, the band contours near the origins are mainly given by the magnitude and the difference of the rotational constants B'_0 and B''_0. Fig. 6 shows the $\Delta v = 0$ sequence of the $a2 \rightarrow X_21$ transition and a simulation of the 0–0 band. Here we used a rotational temperature of 350 K, the theoretical value for B''_0 ($B_0(X_21) = 0.05279$ cm^{-1}), fixed both D_0 values and $q_0(X_2)$ to zero and adjusted the band origin ν_0 and the B_0 value of