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The rotational spectrum of BiO radical in its $X_1\ ^2\Pi_{1/2}$ and $X_2\ ^2\Pi_{3/2}$ states

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Abstract

Rotational spectra have been observed for BiO produced in a DC discharge through a low pressure mixture of O_2, Ar, and Bi vapor. Because of the highly non-thermal distribution of states, it has been possible to observe spectra arising from the $X_1\ ^2\Pi_{1/2}$ level up to $v = 9$ and for the $X_2\ ^2\Pi_{3/2}$ level up to $v = 5$ near $10\,538\ cm^{-1}$. Precise rotational and hyperfine parameters have been determined for the observed states. By using available near infrared (NIR) data in a merged fit, the 0–0 and 1–1 fine structure intervals have been more precisely determined. Although the quality of the fit is very good, the interpretation of the hyperfine constants is complicated by relativistic effects and the interaction of the X_2 state with $A_1\ ^4\Pi_{3/2}$ state. The magnetic and quadrupole coupling constants will be compared with those of the Bi atom and related molecules.

Keywords: BiO radical; Rotational spectra; Hyperfine parameters; Relativistic effects

1. Introduction

BiO has a $^2\Pi_r$ electronic ground state with fine structure interval of $\approx 7087\ cm^{-1}$ between the X_1 and X_2 states. A far reaching study of the BiO radical by Shestakov et al. [1] has provided spectroscopic constants for a total of nine of its electronic states and demonstrated efficient energy transfer from excited molecular oxygen to BiO. Alekseyev et al. [2] have performed extensive relativistic *ab initio* calculations. The rotational constants determined in Ref. [1] for the $X^2\Pi$ state have been used as the basis for a further investigation by microwave spectroscopy at Nobeyama Radio Observatory.

BiO is of particular interest because of the relativistic effects caused by the heavy Bi atom and because of recent interest in the spectra and *ab initio* calculations of the Bi chalcogenides [3,4]. The hyperfine structure of Bi, Bi^+, and Bi^{2+} have been investigated and a number of theoretical treatments have been reported [5–7]. The BiO hyperfine constants determined by this study of the rotational spectrum will provide additional criteria for judging the quality of relativistic *ab initio* calculations for the molecule.

2. Experimental

The millimeter spectrometer used in this work has been described by Kagi and Kawaguchi [8] and Kagi et al. [9]. BiO was produced in a flow system by heating Bi to 1120 K in a Knudsen cell and reacting the resulting vapor with an approximately 1:1 mixture of O_2 and argon in the presence of a dc discharge. A schematic of the apparatus is shown in Fig. 1. A useful side effect of this method of

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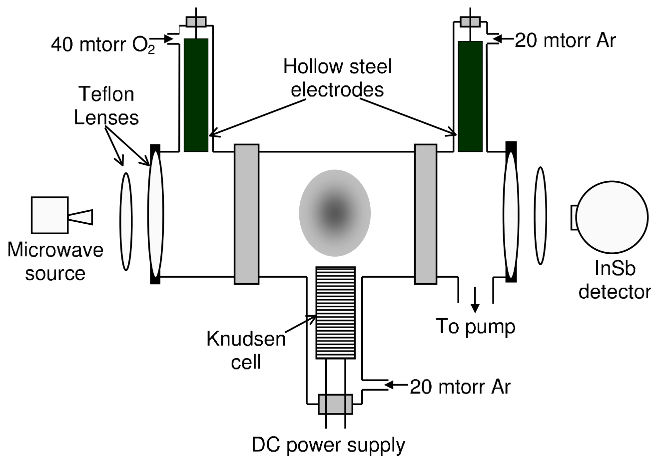

Fig. 1. Schematic drawing of the experimental setup for the production of BiO. See text for details.

production is the population of highly excited vibrational states of BiO. This is presumably due to collisional energy transfer from the metastable $a^1\Delta_g$ electronic state of O_2. As a result, rotational transitions within vibrationally excited levels up to $v \leqslant 9$ in the $X_1\ ^2\Pi_{1/2}$ electronic state and $v \leqslant 5$ in the $X_2\ ^2\Pi_{3/2}$ state have been observed. Degradation of the experimental apparatus due to oxidation of the heating elements prevented searches for the more highly excited states which were observed by Shestakov et al. [1]. A sample microwave spectrum of the BiO radical in the X_1 state is shown in Fig. 2, which illustrates the large Λ doubling as well as the hyperfine pattern that is associated with the presence of the $I = 9/2$ ^{209}Bi nucleus. Fig. 3 shows the characteristic hyperfine pattern associated with the unresolved Λ doublets of the X_2 state. It should be noted that the X_2 states are expected to exhibit very strong Stark effects making the very small splitting of the Λ doublets difficult to observe in the presence of the dc discharge

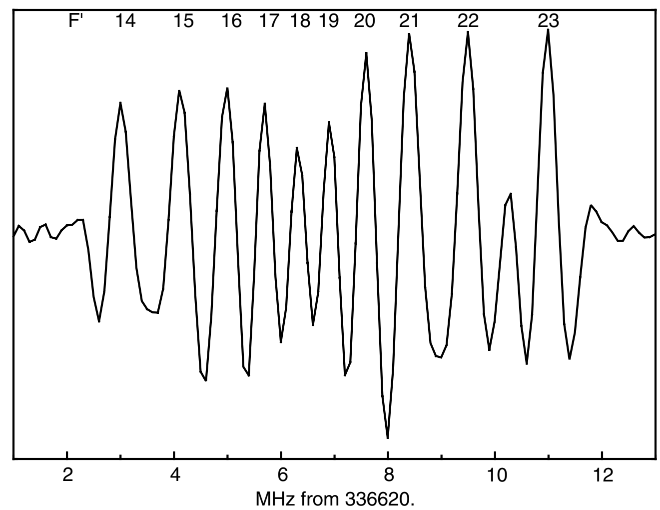

Fig. 3. The $J = 37/2 - 35/2$ transitions of the $X_2\ ^2\Pi_{3/2}$ $v = 0$ state of BiO. The e and f state transitions are unresolved. The baseline has been removed.

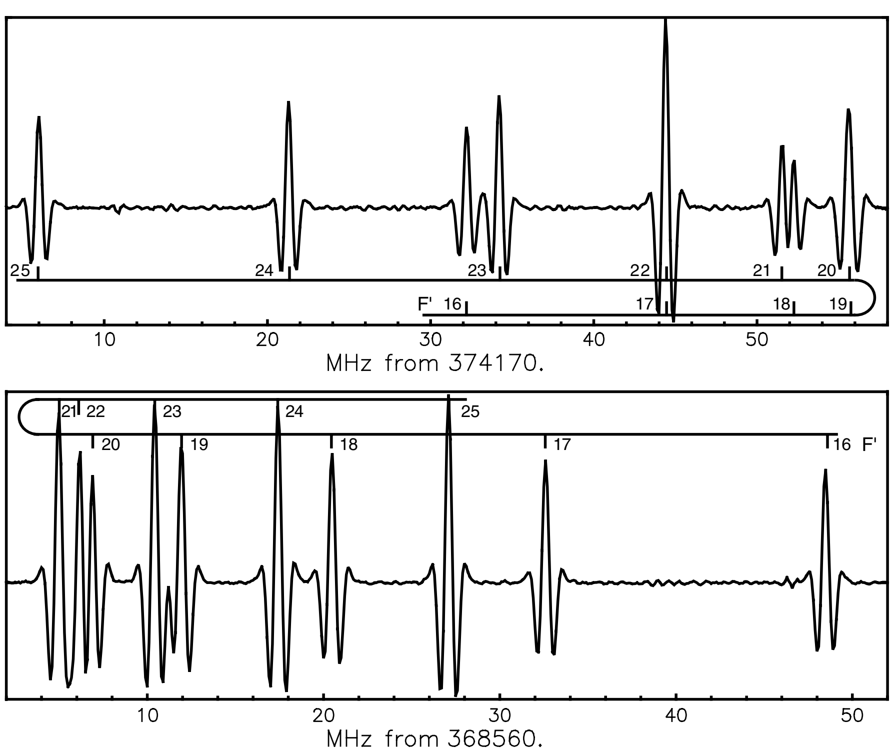

Fig. 2. The $J = 41/2 - 39/2$ transitions of the $X_1\ ^2\Pi_{1/2}$ $v = 0$ state of BiO. The top trace shows f state transitions. The baseline has been removed. See text for details.