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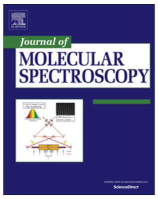

Vibrational energies and full analytic potential energy functions of PbI and InI from pure microwave data

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ABSTRACT

Pure rotational spectra of PbI and InI are interpreted to yield a full analytic potential energy function for each molecule. Rotational spectra for PbI have been retrieved from literature sources to perform the analysis. Rotational transition frequencies for excited vibrational states of InI ($0 < v < 11$) are measured during this work. Ignoring hyperfine splittings, B_v and D_v values are used to generate a set of “synthetic” pure $R(0)$ transitions for each vibrational level. These are then fitted to an “Expanded Morse Oscillator” (EMO) potential using the direct-potential-fit program, **dPOTFIT**. The well-depth parameter, $\mathfrak{D}_e$, is fixed at a literature value, while values of the equilibrium distance r_e and EMO exponent-coefficient expansion (potential-shape) parameters are determined from the fits. Comparison with potential functions determined after including older mid-IR and visible electronic transition data shows that our analysis of the pure microwave data alone yields potential energy functions that accurately predict (to better than 1%) the overtone vibrational energies far beyond the range spanned by the levels for which the microwave data is available.

1. Introduction

Opportunities and advantages presented by broadband rotational spectroscopy are extensively described in a number of publications [1,2]. Amongst these are the opportunity to measure spectra spanning bandwidths exceeding 10 GHz in a single experiment of short duration; and the possibility that spectral patterns can be more easily identified and compared. Many transitions are observed simultaneously and transition intensities reflect intrinsic molecular properties rather than a frequency-dependent instrument design parameter. Each of these advantages is useful in the context that rotational transition frequencies can be simultaneously recorded and compared for many different vibrational states. The ‘conventional’ approach to analyzing such data is to fit those for each vibrational level separately using a program such as Western’s **PGOPHER** [3] to determine distinct values of rotational and hyperfine splitting parameters for each level. This was the first step in the present study. However, other than providing a good estimate of the equilibrium bond length, this provides little insight into the vibrational properties or the potential energy function which governs the molecule’s dynamical behavior. The present work expands on this approach by using the information about the molecule’s dynamical behavior contained in the rotational constants B_v and D_v, and their v-dependence, to determine full analytic potential functions for both PbI and InI.

The microwave spectrum of PbI was recorded recently in our laboratories and presented together with derived geometrical parameters of the molecule in 2014 [4]. In the present work, the extensive results presented in [5] are combined with results obtained by other workers for different wavelength ranges [6–11] and used for the potential energy function fitting described in Section 3.2.2. The microwave spectrum of InI has been explored by several previous works [12,13], with the most recent study having been performed in 2006 [14]. Rotational transition frequencies are measured and parameters in a model Hamiltonian determined for vibrational levels from $v = 4$ to 11 for the first time herein. The present work then combines our new MW results with older electronic transition data for InI in the visible region [15–18] to determine a simple potential energy function (PEF) which provides a

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compact, accurate description of the mechanical behavior of this molecule. It differs from previous studies in that it shows for the first time that it is feasible to determine analytic potential energy functions for PbI and InI from pure rotational data that provide realistic predictions of the vibrational level spacings over an extended domain. In particular, the direct-potential-fits (DPFs) to the microwave data alone are followed by fits to a combination of the microwave data with all available electronic data for these two species to obtain full analytic PEFs that accurately represent all available data for the ground electronic states of PbI and InI. Comparisons between the results of the two types of fit indeed demonstrate that in the absence of any infrared or electronic data, DPF fits to v-dependent microwave data can yield predictions of vibrational level energies that are remarkably accurate on a domain far broader than its v-range.

2. Experimental methods

The broadband microwave spectrum of InI was measured using a chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer fitted with a laser ablation source. Detailed descriptions of the spectrometer and laser ablation source were previously provided in [1,19]. A gas sample containing about 1.5% CF_3I is diluted in argon and prepared at a total pressure of 6 bar. The sample is pulsed into the vacuum chamber of the spectrometer and passes over the surface of a metal rod that is ablated by a Nd:YAG laser pulse ($\lambda = 532$ nm), pulse duration of 10 ns, pulse energy of 20 mJ) before undergoing supersonic expansion. A repetition rate of approximately 1.05 Hz is employed. The rod is continually translated and rotated in order to expose a fresh surface to each laser pulse.

The sequence employed to record broadband microwave spectra involves: (i) polarization of the sample by a microwave chirp that sweeps from 6.5 to 18.5 GHz within 1 μs, and (ii) recording of the free induction decay of the molecular emission over a subsequent period of 20 μs. The sequence of (i) and (ii) is repeated eight times within the (about 200 μs) period of the gas nozzle pulse which introduces sample gas into the spectrometer. The free induction decay (FID) of the polarization is digitized using a 25 Gs/s digital oscilloscope after down-mixing against a 19 GHz local oscillator. The time-domain data are averaged to improve the S/N of recorded spectra. Individual transitions are observed with full width at half maximum (FWHM) of 150 kHz after time-domain data are Fourier transformed using a Kaiser-Bessel digital filter. 44 k FIDs were averaged in order to record the spectrum of Fig. 1.

3. Results

3.1. Assignment of the rotational spectra of vibrational excited states of InI

Components of the prepared gas sample were probed while undergoing supersonic expansion to reveal rotational transitions of CF_3I and IF in addition to those of InI. Assignments of rotational transitions in the $v = 0$, 1, 2 and 3 states of the latter were readily achieved through reference to previous studies [12,13]. A section of the spectrum displaying rotational transitions of InI for a series of vibrational states is displayed in Fig. 1. The relative intensities of the rotational spectra of the excited vibrational states correlate with the ratio of the vibrational state populations. However, the vibrational temperature implied by this ratio does not necessarily provide a good indication of all energy partitioning between vibrational, rotational and translational modes. The events that follow the pulsed laser vaporization of the rod target proceed under conditions that do not allow components of the gas sample to equilibrate. The conditions employed are apparently particularly favorable to the generation of excited vibrational states of PbI and InI. Excited vibrational states are commonly observed in spectra recorded for molecules generated through a combination of laser vaporization and supersonic expansion [20–23].

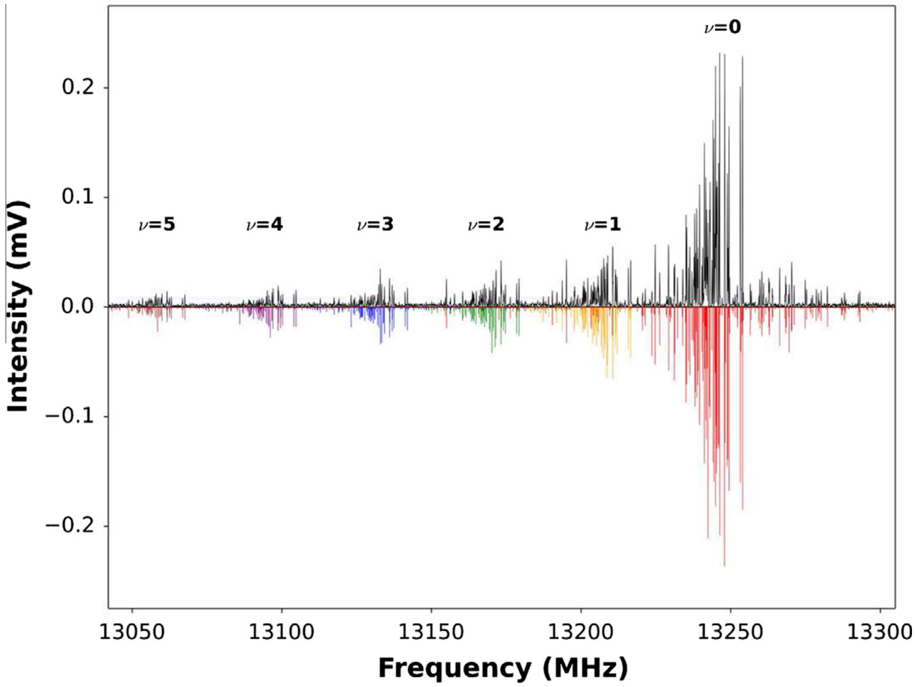

Fig. 1. A section of the rotational spectrum recorded for InI displaying transitions in a series of vibrational states. The experimentally-measured spectrum is displayed in black. Simulated $J' \rightarrow J'' = 7 \rightarrow 6$ transitions in $v = 0$ (red), $v = 1$ (orange), $v = 2$ (green), $v = 3$ (blue), $v = 4$ (purple) and $v = 5$ (gray) states are constructed from fitted values of spectroscopic parameters (see Table 1) and are displayed inverted. 44 k FIDs were averaged to record the displayed spectrum (data collected over about 3 h of real time). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)