A theoretical contribution to the characterization of the low-lying electronic states of BeBr including spin–orbit effects

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ABSTRACT

Electronic states of BeBr correlating with the first two dissociation channels are investigated at a high level of electronic structure theory (CASSCF/MRCI) along with quintuple-zeta quality basis sets. Very reliable potential energy curves are constructed and regions of both avoided and curve crossings that greatly resemble the ones for BeCl are identified. For both the ground state ($X\ ^2\Sigma^+$) and the first excited one (A $^2\Pi$), this study corroborates the present still limited experimental knowledge about this system and significantly extends its spectroscopic characterization. For the three doublets in the interval between 30 000 and 40 000 cm^{-1}, the inclusion of spin–orbit effects neatly accounts for the interactions between the relativistic states. For the A $-$ X band system, transition moments were evaluated and transition probabilities, as expressed by the Einstein emission coefficients, computed; radiative lifetimes completed the characterization of the A state. The C $^2\Sigma^+$ state was found to have two minima in the $\Lambda + S$ representation, the first one with just one vibrational level; this shallow potential then disappears when perturbations by the B $^2\Pi$ and the a $^4\Sigma^+$ states are taken into account.

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1. Introduction

Of the three species in the series of beryllium monohalides, BeF, BeCl, and BeBr, the beryllium monobromide molecule is the one least known experimentally. In a brief note by Reddy and Rao [1], the first report on a BeBr investigation dates back to 1967, with the observation of a bluish color emission when a mixture of bromine and argon was passed over warm beryllium metal powder and attributed to transitions in BeBr. Later expanded in an article [2], the authors describe three sequences of bands degraded to longer wavelengths in the region of 3660–3920 Å. In analogy with the already known spectra of BeF and BeCl, they attributed the bands to transitions of the A $^2\Pi$ – X $^2\Sigma^+$ system, and reported vibrational quantum formulae representing the Q_1, R_1, and R_2 heads. A reinvestigation of BeBr by Reddy et al. under high dispersion, including isotope shift analysis, provided next a more accurate set of spectroscopic constants for the X and A states [3]. A rotational analysis study on the 0–0 band of the A $^2\Pi$ – X $^2\Sigma^+$ system, performed by Carleer et al. [4], resulting in the determination of the internuclear distance R_0 and the rotational constant B_0 for both X $^2\Sigma^+$ and A $^2\Pi$ states, the spin–orbit coupling constant for the A $^2\Pi$ state, and the transition energy (T_{00}) was the only other reference to an experimental investigation on BeBr, to the best of our knowledge. Concerning the experimental difficulties of carry-

ing out a rotational analysis of bands of BeBr at the time, Carleer et al. noted that besides the need of a very high resolution spectrograph, this system in particular has very similar vibrational constants for both the X $^2\Sigma^+$ and A $^2\Pi$ states, thus leading to a strongly overlapping sequence of bands. In addition, the nearly equal abundance of two of the bromine isotopes doubled the number of branches to be analyzed. An estimate of the dissociation energy of BeBr (D_0 = 71 kcal mol^{-1}) based on a correlation of thermochemical properties across the entire alkaline earth halide series was reported by Kleinschmidt and Hildenbrand [5]; this value differs significantly from the empirical determination of Reddy et al., 91.31 kcal mol^{-1} [6]. Theoretically, not a single study on the electronic states of BeBr has been found in the literature, with the exception of an early attempt at estimating theoretically the intensities of A $^2\Pi$ – X $^2\Sigma^+$ transitions by Kuz'menko and Chumak [7] through the calculation of Franck–Condon factors using a Morse potential energy function.

In contrast to BeBr, beryllium monochloride (BeCl) has been more thoroughly investigated in the literature both experimentally and theoretically, as recently reported by Lima and Ornellas [8]. Although the electronic states of BeBr are expected to show close similarities to those of BeCl, a reliable theoretical investigation of its electronic structure and spectroscopic parameters is certainly warranted. In this work, our major focus is the characterization of the electronic states of BeBr in a manner similar to that already done for BeCl [8]. Potential energy curves for a manifold of low-lying electronic states, including spin–orbit interactions, are

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constructed that can account in a reliable way for the observed and the as yet not observed electronic spectra of this species, especially the characterization of regions of avoided crossings, and crossings that can lead to predissociation. Besides the determination of spectroscopic parameters, we also evaluated the transition moment function, and radiative transition probabilities for $A - X$ transitions, as estimated by the Einstein emission coefficients $A_{v'v''}$; radiative lifetimes of vibrationally excited states of the A $^2\Pi$ state were also estimated. By quantitatively accounting for the properties of this system, the present study is expected to provide an accurate global picture of a manifold of electronic states of BeBr, and thus reliable data to guide further experimental spectroscopic investigations.

2. Methodology

In analogy with our previous study on the BeCl system, the focus of this investigation is the set of states of BeBr correlating with the lowest-lying dissociation channel, Be (^1S_g) + Br (^2P_u), namely, $^2\Sigma^+$ and $^2\Pi$, and those leading to the second dissociation channel, Be (^3P_u) + Br (^2P_u), associated with the atomic states $^{2,4}\Sigma^+$ (2), $^{2,4}\Sigma^-$, $^{2,4}\Pi$ (2), and $^{2,4}\Delta$, according to the Wigner–Witmer rules [9].

In order to account simultaneously for bond breaking of the ground and excited states, a two step process involving first a state-averaged complete active space self-consistent (SA-CASSCF) [10,11] calculation followed by another one of the multireference configuration interaction (MRCI) type was the basic theoretical method used to describe the electronic structure of this system. The MRCI calculation used the internally contracted approach as implemented in the Molpro-2009 suite of programs [12–14]. In this latter step, we have correlated the 1s electrons of the Be atom but not included the 1s orbital in the active space of the CASSCF calculation. In the SA-CASSCF calculation all possible distributions of nine electrons in nine orbitals comprising the active space (5,2,2,0) were allowed. Besides the valence orbitals, the active space includes one extra orbital of A_1 symmetry to increase the flexibility of the reference space and thus to improve the quality of the wavefunction in regions of avoided crossings identified in test calculations. This notation implies that the orbitals transform according to the irreducible representations (A_1, B_1, B_2, A_2) of the C_{2v} point group, since most computer programs use Abelian subgroups to classify the orbitals and electronic states. The correspondence between the representations in the $C_{\infty v}$ and C_{2v} point groups is: $A_1(\Sigma^+, \Delta)$, $B_1(\Pi_x)$, $B_2(\Pi_y)$, $A_2(\Sigma^-, \Delta)$. In the SA-CASSCF step we mixed five states of A_1 symmetry, four states of B_1 and B_2 symmetries, and two states of A_2 symmetry.

For this choice of active space, the dimension of the reference space resulted in 2308 (1408) configuration state functions (CSF) for the doublet (quartet) states of A_1 symmetry, 2200 (1440) for those of B_1 and B_2 symmetries, and 2112 (1472) for the ones of A_2 symmetry. In the MRCI step, the configuration space ranged from about 4.0 to 7.5 million CSF for the doublets, and 2.0–3.1 million for the quartets. The molecular orbitals used to construct the N-particle basis are in fact state-averaged natural orbitals obtained by the diagonalization of an average density matrix for each one of the spin symmetries. In the expansion of the molecular orbitals, we used the set cc-pwCV5Z for beryllium [15] and aug-cc-pV5Z bromine [16], briefly V5Z.

Total energies were evaluated at about 60 internuclear distances and used to generate a numerical potential for the nuclear motion by the interpolation of about 2000 distances. This potential was next used in the solution of the Schrödinger radial equation by the Numerov–Cooley method as implemented in the Intensity Program [17], thus allowing the determination of vibrational energies, vibrationally averaged properties, and transition probabilities. The total energies used to generate the potential for the nuclear motion

were corrected by an estimate of the contribution of the missing higher excitations needed to reach the full configuration interaction limit known as the Davidson correction (+Q) [18,19]. In the determination of spectroscopic parameters, we have used standard fitting procedures as described in previous studies [20–23].

Einstein spontaneous emission coefficients, $A_{v'v''}$ (in s^{-1}), were evaluated by the expression given below for the case of rotationless potentials

$$A_{v',v''} = 7.2356 \times 10^{-6} |D_{v',v''}|^2 v_{v',v''}^3 \frac{(2 - \delta_{0,\Lambda'+\Lambda''})}{(2 - \delta_{0,\Lambda'})}$$

and used to estimate radiative transition probabilities. Here, $v_{v',v''}$ is the transition energy, and $(2 - \delta_{0,\Lambda'+\Lambda''})/(2 - \delta_{0,\Lambda'})$ is the degeneracy factor [24,25]. The multiplication constant is the appropriate factor to express the probabilities in s^{-1}, when the transition moment is given in units of eÅ, and the energy in cm^{-1}. In this expression, $D_{v',v''}$ stands for the transition dipole moment operator matrix element evaluated as

$$D_{v',v''} = \langle v'|D(R)|v'' \rangle$$

where $|v'\rangle$ and $|v''\rangle$ represent the upper and lower state vibrational wavefunctions, and $D(R)$ is the transition dipole moment function evaluated over the whole range of internuclear distances at the MRCI level of theory. As usual, radiative lifetimes were evaluated as the inverse of the total Einstein A_v coefficients, which implies summing the transition probabilities to all lower vibrational states in all lower electronic states. In the evaluation of transition probabilities, we considered the recommendations given by Whiting et al. [26]. In this respect, the concise report by Larsson [27] summarizes for the reader the various conversion factors between the transition moment and other dynamical variables.

Finally, to estimate spin–orbit effects on the energies we have used the interacting states method with the spin–orbit matrix elements evaluated with the one- and two-electrons Breit–Pauli operators [28] at the MRCI level of theory along a quadruple-zeta quality basis set; this calculation also correlated the 1s electrons of beryllium. As implemented on the Molpro-2009 package, the spin–orbit eigenstates were obtained by diagonalizing the matrix representation of the $H_{el} + H_{SO}$ operator, constructed by the replacement of the diagonal elements of $H_{el} + H_{SO}$ matrix by the corresponding MRCI + Q/V5Z values.

3. Results and discussion

3.1. Potential energy curves, vibrational energies, and spectroscopic parameters

The profiles of the potential energy curves (PEC) of the doublet and quartet $\Lambda + S$ states here investigated are depicted in Fig. 1, and for the bound ones the associated sets of spectroscopic parameters are summarized in Table 1. For the ground (X $^2\Sigma^+$) and the first excited (A $^2\Pi$) states for which very accurate experimental data on the internuclear distance R_0 have been determined by Carleer et al. [4], 3.6911 a_0 (1.9532 Å) and 3.7351 (1.9765 Å), respectively, this study predicts equilibrium distances (R_e) of 3.694 a_0 (1.955 Å) and 3.731 a_0 (1.975 Å) in very good agreement with the experimental results. As to the excitation energy (T_{00}), we have obtained 26 654 cm^{-1} (see discussion below), a value also in good accord with that reported by Carleer et al., 26437.6 cm^{-1} [4]. Concerning the vibrational constants (ω_e, $\omega_e x_e$) for the species Be^{79}Br, our estimates are (715.9, 3.592 cm^{-1}) for the ground state X $^2\Sigma^+$, and (700.0, 3.492 cm^{-1}) for the state A $^2\Pi$. Comparison of these results with the available experimental data for the Q_1 band head reported by Reddy et al. [3], (715.06, 4.30) and (702.29, 3.98), also shows a very good agreement. As another check of the