Temperature Dependence of HeBr₂ Isomers' Stability Through Rovibrational MCTDH Calculations

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Abstract

The multiconfiguration time-dependent Hartree (MCTDH) method using a six-dimensional Hamiltonian that includes all rotational and vibrational degrees of freedom and an *ab initio* potential energy surface was employed to calculate the rovibronic states of the HeBr₂ van der Waals complex. All rotational states of energies within 7 cm⁻¹ with respect to the energy of the linear ground state were calculated without restriction of the total angular momentum. In total, we obtained 500 and 320 rotationally excited states of the ground vibrational T-shaped and linear isomers of the HeBr₂, respectively, and compared them with those predicted by the rigid rotor model. A thermodynamic model was then introduced to determine the relative stability of the two conformers as a function of the temperature. On the basis of the present results, the linear conformers were found to be energetically more stable than the T-shaped ones by 1.14 cm⁻¹ at T=0 K, while conversion from linear to T-shaped complexes was observed at temperatures above 2.87 K.

Introduction

Over the last decades, there has been an extensive interest in studying van der Waals (vdW) complexes formed by rare gas atoms and dihalogen molecules.¹ Due to the richness of processes involved in their dynamics, high resolution spectroscopy techniques have provided valuable information for such vdW complexes, which represent ideal systems to test new approaches and theoretical tools.²⁻⁴ From the theoretical side, the study of these weakly bound complexes has been enforced by the development of *ab initio* methods and the huge increase of computational resources. Thus, they are presenting a perfect scenario for the interaction of theory and experiment in the study of the long-range intermolecular forces, energy transfer mechanisms or solvation structures.⁵⁻¹⁰

It is known that, the triatomic vdW complexes, formed by a homonuclear dihalogen molecule and a rare gas atom, exhibit a double minimum topology in their potential energy surface.^{3,11-16} Interestingly, in the case of He-dihalogen complexes, such as HeI₂ and HeBr₂, their well-depth difference counts to few cm⁻¹, with the linear well being the deepest, while the energy differences

between the corresponding linear and T-shaped isomers, due to the zero-point effects, is just about 1 cm^{-1} .^{5,13–15,17–19} We should note that the quantum mechanical interpretation of such vdW isomers, that are normally very floppy with wave functions spanning wide regions of configuration space, is based on the localization of one or more specific quantum states in the region of the global or other local potential minima and, in this sense, is often very unclear. Recent spectroscopic evidences have also supported the existence of both linear and T-shaped isomers for these vdW complexes.^{1,9,12–14,20,21} However their relative stability was not always in accord with the theoretical predictions, or even with the measurements of different sets of experiments. Discrepancies between experimental data have been attributed to saturation effects and non-equilibrium populations of the isomers,²² while the small differences with *ab initio*-based quantum calculations have been initially attributed to the topology and accuracy of the underlying PES.¹⁵ Moreover, the temperature may also play an important role in the relative stability of the two isomers,¹⁵ as it can clearly influence the population of the two different vdW conformers in a supersonic beam expansion, as the less energetic rotational levels are occupied, even at low temperatures. Although, as a number of experimental studies have detected different isomers of vdW complexes in supersonic expansions,^{9,13,21} questions about the mechanisms for their formation, as if they all formed in thermodynamic equilibrium, and how their relative populations change within the expansion, are still open.

Most of the previous theoretical studies on such triatomic vdW complexes are restricted to some low fixed values of the total angular momentum and at zero temperature. In particular, in the work by Boucher *et al.* quantum mechanical calculations have been performed for total angular momenta $J > 9$ to calculate the rovibronic spectra of HeBr_2 ,¹³ aiming to check the potential surface, and compare their results with our previous data for $J = 0$.¹⁸ In this work, a different approach is adopted taking advantage of the capabilities of the MCTDH method^{23,24} to perform for the first time a six dimensional (6D) quantum calculation for a triatomic weakly-bound molecule including all vibrational and rotational degrees of freedom. Thus, we first derived the exact kinetic energy operator for a triatomic bent molecule, that can also serve for studying molecules in em-

bedded or confined environments. In turn, we calculate all the rotational states of energies within 7 cm^{-1} ($\sim 10\text{ K}$) with respect to the linear ground state for each of the HeBr_2 conformers without restriction of the total angular momentum. The calculated energies and states are then used along a thermodynamical model²² to study the temperature dependence of the relative population for the linear and T-shaped conformers. The results presented here show that the conversion between the two different isomers of the HeBr_2 complex can occur above specific temperature values.

The article is organized as follows: In the next section a description of the computational details of the MCTDH calculations is made together with the resulting ground and rotationally excited states. Then, a description of the thermodynamical model used is presented and the results for the crossing temperature of the population of the conformers is shown. The article ends with the summary and concluding remarks.

Computational Methods, Results and Discussion

Hamiltonian Operator

We use Jacobi coordinates (see Figure 1) to describe the molecule, with $\mathbf{r}$ being the vector joining the two Br atoms and $\mathbf{R}$ the vector from the center of the Br_2 molecule to the He atom. γ is the angle between the vectors $\mathbf{r}$ and $\mathbf{R}$. The Z axis of the body-fixed frame is chosen to be parallel to $\mathbf{R}$ and $\mathbf{r}$ is lying in the XZ -plane. So the final set of coordinates are $(r, R, \gamma, \phi, \theta, \chi)$ with (ϕ, θ, χ) being the three Euler angles connecting the body-fixed and space-fixed frames.

Following the procedure described in Ref.²⁵ the kinetic energy operator is derived in these

Figure 1: Schematic representation of the Jacobi Coordinates (r, R, γ) for the HeBr₂ system, together with the three Euler angles (ϕ, θ, χ) connecting the space-fixed (SF) and body-fixed (BF) frames.

coordinates, and the Hamiltonian operator $\hat{H}$ reads:

$$\begin{aligned}
 \hat{H} = & -\frac{\hbar^2}{2} \left[\frac{1}{\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{m} \frac{\partial^2}{\partial r^2} \right. \\
 & + \left(\frac{1}{\mu R^2} + \frac{1}{mr^2} \right) \frac{\partial^2}{\partial \gamma^2} + \left(\frac{1}{\mu R^2} + \frac{1}{mr^2} \right) \cot(\gamma) \frac{\partial}{\partial \gamma} \\
 & + \frac{1}{\mu R^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{\mu R^2} \cot(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\mu R^2} \csc^2(\theta) \frac{\partial^2}{\partial \phi^2} \\
 & + \left(\frac{1}{mr^2} \csc^2(\gamma) + \frac{2}{\mu R^2} \cot(\gamma) \cot(\theta) \cos(\chi) + \frac{1}{\mu R^2} \cot^2(\gamma) + \frac{1}{\mu R^2} \cot^2(\theta) \right) \frac{\partial^2}{\partial \chi^2} \\
 & + \frac{2}{\mu R^2} \cot(\theta) \sin(\chi) \frac{\partial^2}{\partial \gamma \partial \chi} - \frac{2}{\mu R^2} \csc(\theta) \sin(\chi) \frac{\partial^2}{\partial \phi \partial \gamma} \\
 & + \left(-\frac{2}{\mu R^2} \cos(\chi) \cot(\gamma) \csc(\theta) - \frac{2}{\mu R^2} \cot(\theta) \cos(\theta) \right) \frac{\partial^2}{\partial \phi \partial \chi} \\
 & \left. + \frac{2}{\mu R^2} \cot(\gamma) \sin(\chi) \frac{\partial^2}{\partial \theta \partial \chi} - \frac{2}{\mu R^2} \cos(\chi) \frac{\partial^2}{\partial \theta \partial \gamma} \right] + V(r, R, \gamma)
 \end{aligned}$$

(1)

where m is the reduced mass of the Br_2 system, μ is the reduced mass of the He-Br_2 complex and the corresponding potential $V(R, r, \gamma)$ is represented by the potential form:

$$V(r, R, \gamma) = V_{\text{Br}_2}(r) + V_{\text{HeBr}_2}(r, R, \gamma).$$

The three-body $V_{\text{HeBr}_2}(r, R, \gamma)$ term corresponds to a CCSD(T) parameterized potential for the HeBr_2 complex,¹⁸ while $V_{\text{Br}_2}(r)$ represents the diatomic interaction Br-Br potential from refs.^{18,26}

MCTDH Calculations

All calculations were carried out with the Heidelberg MCTHD package of codes.²³ In Table 1, the primitive basis set used in the MCTDH calculations is shown, where *sin* stands for the sine discrete variable representation (DVR) basis, *HO* refers to the harmonic oscillator DVR basis, *Leg* stands for the Legendre DVR basis and *exp* for the exponential DVR basis.

Table 1: Type, number and range of the primitive DVR basis set²³ used in the MCTDH calculations.

Coordinate	DVR	N ^o	Range
$r(\text{\AA})$	<i>sin</i>	35	(2.10,2.46)
$R(\text{\AA})$	<i>HO</i>	41	(2.50,7.50)
$\gamma(\text{rad})$	<i>Leg</i>	61	(0, π)
$\phi(\text{rad})$	<i>exp</i>	31	(0,2 π)
$\theta(\text{rad})$	<i>Leg</i>	31	(0, π)
$\chi(\text{rad})$	<i>exp</i>	31	(0,2 π)

The POTFIT method is used to write the $V_{\text{HeBr}_2}(r, R, \gamma)$ potential term as a sum of products of single-particle operators. The contraction is constructed over the angular coordinate γ , and 20 natural potentials are used in the POTFIT calculations for the R and r coordinates. In these calculations we considered the relevant region below 20 cm^{-1} with a root mean square (rms) error of the fit in this region smaller than 0.001 cm^{-1} .

The lowest states in the linear and T-shaped conformations are calculated using the 6D Hamiltonian shown in Eq. 1, and the *improved relaxation* method (IR), implemented in the MCTDH

code. In Table 2 we show the number of SPFs employed for these IR calculations. The ground vibrational state values of $E_0^L = -16.03 \text{ cm}^{-1}$ and $E_0^T = -14.89 \text{ cm}^{-1}$ below the dissociation energy of He+I₂ are obtained for the linear and T-shaped configurations, respectively. These values are in excellent agreement with the previously reported values of -16.03 and -14.92 cm^{-1} obtained using the MCTDH program and the same potential energy surface using the 3-dimensional Hamiltonian with zero total angular momentum ($J=0$),¹⁹ as well as within the convergence error of 0.01 cm^{-1} compared to the 3D variational calculations.¹⁸ In Figures 2 and 3 (see inner panels) we plot the distribution probabilities in the Cartesian ZX-plane of the ground states for the linear and T-shaped conformers, respectively, together with the equipotential curves of the underlying PES. We should note that the potential well-depths are 48.70 and 40.19 cm^{-1} at linear and T-shaped configurations, respectively, with an energy difference between them of 8.51 cm^{-1} . As in previous studies on the HeBr₂,^{13,18,19} one can see that the distribution probabilities of the lowest vibrational states are found confined in either the linear or the T-shaped wells (see Figs. 2 and 3), so we can consider two different isomers of the ground state HeBr₂ complex, with the linear one being more stable by 1.14 cm^{-1} than the T-shaped isomer.

In turn, we use the *block improved relaxation* method (BIR) implemented in the Heidelberg MCTDH package,^{27,28} to calculate the rotationally excited states of each conformer. From the BIR calculations we compute 320 and 500 states for the linear and T-shaped species, respectively, that cover energies up to 7 cm^{-1} above the global E_0^L energy. In Table 2 we show the combination mode scheme and the number of SPFs used in these MCTDH calculations. All of them are full dimensional (6D) calculations, with no restriction of the total angular momentum J , and each state has a $2J + 1$ energy level degeneracy.

In Figures 2 and 3 we plot the energy of the calculated states as a function of the index number N of rotational energy levels, up to 320 and 500 for the linear and T-shaped conformers, respectively. States that mix both conformers appear $\sim 7.0 \text{ cm}^{-1}$ above the global ground state energy E_0^L .¹⁸ Thus, in Figures 2 and 3 only states with energies below -9.0 cm^{-1} , corresponding the lowest 238 and 496 states for the linear and T-shaped conformers, respectively, were considered, showing

Table 2: Combination mode scheme and number of SPFs used in the IR and BIR calculations for each conformer.

Mode	SPFs in IR	SPFs in BIR
		Linear/T-shaped
N_r	1/1	1/1
$N_{R,\gamma}$	12/12	10/5
N_θ	11/11	30/22
$N_{\chi,\phi}$	45/45	250/250

a much more congested spectrum for the T-shaped configurations. In Tables 3 and 4 we present the energy values and the degeneracies of the calculated states and compare them to the rigid rotor (RR) states.²⁹

By calculating the rotational constants A_{rot} , B_{rot} , and C_{rot} with respect to the three principal moments of inertia, I_a , I_b and I_c , we can distinguish the type of rigid rotor and estimate the corresponding rotational energy levels. Thus, for $J = 1$ there are $2J + 1 = 3$ different K levels, which in the case of an asymmetric rotor ($I_a < I_b < I_c$) have rotational energies of $A + B$, $A + C$ and $B + C$, respectively, while for a prolate symmetric top ($I_a < I_b = I_c$) are $2A$ for $K = 0$ and $A + C$ for the doubly degenerate $K \neq 0$ levels. Thus, a near prolate symmetric model is employed for linear states, while a near T-shaped asymmetric rotor is used for the T-shaped states. In Figure 2 we display the rotational energy values for the linear states as a function of their index number, while in Table 3 we list the lowest energy value of each group of $2J + 1$ degenerated states and their degeneracy up to $J = 10$. The energy difference between the two extreme levels for each J is found to be less than 2% of the excitation energy value, except for the highest rotational levels, corresponding to $J = 9$ and $J = 10$, that were harder to converge with our computational capabilities. The rotational constant, $B_{rot}^L = 0.057 \text{ cm}^{-1}$, is calculated as half the energy difference between the ground ($J = 0$) and first rotational excited level ($J = 1$) from our MCTDH results. One can also note in Table 3 the validity of the rigid rotor model for the linear HeBr₂ molecule, and the excellent agreement with the calculated MCTDH rotational levels. In turn, we also use the results presented in Table 4 for $J = 0$ and $J = 1$ to calculate the rotor constants for the T-shaped conformers $A_{rot}^T = 0.271 \text{ cm}^{-1}$, $B_{rot}^T = 0.082 \text{ cm}^{-1}$ and $C_{rot}^T = 0.062 \text{ cm}^{-1}$. Based on the degeneracy of $2J + 1$ we assign the states

corresponding to $J \leq 4$ shown in Table 4. Higher values of J are more difficult to assign due to the larger congestion of states for the T-shaped species. Again, the agreement between the energy values corresponding to an asymmetric rigid rotor model and the 6D MCTDH results are remarkable, justifying a rigid rotor model for assigning both linear and T-shaped rotational states for the HeBr_2 .

Table 3: Energies of the lower rotational states for the linear isomer with respect to the ground state located at $E_0^L = -16.03 \text{ cm}^{-1}$.

J	Degeneracy	MCTDH (cm^{-1})	RR (cm^{-1})
0	2	0.000	0.000
1	6	0.114	0.114
2	10	0.341	0.341
3	14	0.681	0.681
4	18	1.135	1.136
5	22	1.702	1.703
6	26	2.388	2.385
7	30	3.196	3.179
8	34	4.128	4.088
9	38	5.183	5.110
10	42	6.386	6.245

Thermodynamic Model

Following Ref. 22 we implemented the thermodynamic model described therein to investigate the populations of linear and T-shaped HeBr_2 vdW complexes. We also assume that both isomers are in thermodynamic equilibrium, as they are separated by high enough potential barriers, and that the ratio of their populations at a given temperature is equal to the ratio of their partition functions at the same temperature. Further, vibrational and rotational motions of the HeBr_2 in its ground electronic state are reasonably well separated, as vibrational energies are greater than the rotational constants, allowing the factorization of the partition functions as:²²

$$Z^{L,T}(T) = Z_{vib}^{L,T}(T) Z_{rot}^{L,T}(T) \quad (2)$$

Table 4: Energies of the lowest rotational states for the T-shaped isomer with respect to the ground state for the T-shaped conformed located at $E_0^T = -14.89 \text{ cm}^{-1}$.

J	Degeneracy	MCTDH (cm^{-1})	RR (cm^{-1})
0	1	0.000	0.000
1	3	0.144	0.143
		0.333	0.333
		0.353	0.353
2	5	0.428	0.429
		0.598	0.599
		0.660	0.660
		1.226	1.228
		1.230	1.230
3	7	0.850	0.853
		0.993	0.999
		1.119	1.120
		1.655	1.658
		1.662	1.666
		2.649	2.657
		2.658	2.657
4	9	1.407	1.412
		1.520	1.529
		1.729	1.730
		2.222	2.231
		2.245	2.253
		3.219	3.233
		3.219	3.233
		4.608	4.626
		4.612	4.626

with Z_{vib} and Z_{rot} denoting the vibrational and rotational partition functions, respectively. The ratio between the vibrational partition functions can be written as:

$$\frac{Z_{vib}^T(T)}{Z_{vib}^L(T)} = \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (3)$$

where $\Delta E = E_0^T - E_0^L = 1.14 \text{ cm}^{-1}$.

Figure 2: Energy of the rotationally excited energy levels for the linear conformer as a function of the index number N. A plot of the density distribution is also presented in the inner frame.

Figure 3: Energy of the rotationally excited energy levels for the T-shaped conformer as a function of the index number N. A plot of the density distribution is also presented in the inner frame.

The value for $Z_{rot}^{L,T}$ is given by:

$$Z_{rot}^{L,T} = \sum_i \exp\left(-\frac{E_i^{L,T}}{k_B T}\right) \quad (4)$$

where i runs over the calculated states shown in Figures 2 and 3 and $E_i^{L,T}$ denotes the energy of each state.

In Figure 4 we present the calculated partition functions from the MCTDH results for the linear (see upper panel) and T-shaped (see lower panel) conformers as a function of the temperature. Once again, for the linear conformer the partition function corresponding to a symmetric top rigid rotor,^{12,30}

$$Z_{rot}^L(T) = \frac{k_B T}{B_{rot}^L} \quad (5)$$

where $T \gg \theta_{rot}^L = B_{rot}^L/k_B = 0.082$ K, with θ_{rot}^L being the rotational characteristic temperature of the linear conformer. For the T-shaped conformer, the theoretical approximation of the rotational partition function is based on the asymmetric top rigid rotor,^{12,30}

$$Z_{rot}^T(T) = \frac{\pi^{1/2}}{2} \left(\frac{k_B^3 T^3}{A_{rot}^T B_{rot}^T C_{rot}^T} \right)^{1/2} \quad (6)$$

with $T \gg \sqrt[3]{B_{rot}^L A_{rot}^T C_{rot}^T}/k_B = 0.160$ K. One can see that both characteristic temperatures are much lower than the temperature of the cluster, justifying in this way the approximation made.

In Figure 4 the partition functions obtained from the rigid rotor (RR) model are also shown as a function of temperature. One can see a very good accord with the MCTDH results up to temperatures of around 3 and 2.5 K for the linear and T-shaped cases, respectively. Beyond these temperature values the effect of the finite number of states in the MCTDH calculations begins to be important and the rotational partition functions diverge with the increasing temperature. Nevertheless, the vibration term in Eq. 3 for the T-shaped conformer helps to delay the divergence in the total partition function.

In Figure 5 we plot the relative partition functions, $Z^{L,T}/Z^{TOT}$, as a function of the temperature. One can see that the populations curves of the two conformers cross at 2.87 K for the calculated MCTDH partition functions and 2.66 K using the RR model. The LIF spectra of the linear and T-shaped He...⁷⁹Br₂ complexes have been recorded by Boucher *et al.*¹³ In all the Br₂ B – X spectral

regions studied they have observed that the peak intensity of the T-shaped feature decreases and that of the linear one increases with decreasing temperature. Thus, by fitting the intensity ratio of their experimental data for the linear and T-shaped species obtained from the 12–0 LIF spectra of He...⁷⁹Br₂ as a function of inverse temperature, T^{-1} , for T values between 0.25 and 1 K, they also provide an experimental estimate of $\Delta E=0.4\text{ cm}^{-1}$. This value is smaller than the theoretical value of $\Delta E=1.14\text{ cm}^{-1}$, obtained from *ab initio* quantum mechanical calculations. As expected the $Z^L(T)/Z^T(T)$ ratio shows a high sensitivity to the binding energy difference, ΔE , between the two isomers, and it is also expected to affect the value of the crossing T_C temperature. Thus, by considering the calculated MCTDH rotational excitation energies and the experimental predicted ΔE of just only 0.4 cm^{-1} , we then obtained the crossing point temperature for $T_C=1.60\text{ K}$, while in Figure 6 we show the dependence of T_C as a function of the ΔE values between 0.4 and 1.2 cm^{-1} . One can see that the same $T_C=1.60\text{ K}$ value is also estimated using the RR model for $\Delta E=0.4\text{ cm}^{-1}$, while for higher binding energy differences T_C increases and larger deviations are found, as it should be expected from the agreement shown in Figure 4 of the rotational partition functions at that temperatures.

Summary and Conclusions

The ground and rotational excited states of the HeBr₂ van der Waals complex have been calculated for the linear and T-shaped conformers using a 6D model that does not restrict the quantum total angular momentum number J . The HeBr₂(X) vdW complex was chosen as a test case, for which there are experimental evidence of coexistence of both linear and T-shaped isomers. The ground state energies of $E_0^L=-16.03\text{ cm}^{-1}$ and $E_0^T=-14.89\text{ cm}^{-1}$ for such linear and T-shaped conformers, respectively, are computed, and are found in very good agreement with previous results using a 3D model for the $J=0$ case. Totally, 320 rotationally excited states for the linear conformer and 500 states for the T-shaped one were calculated. Their $2J+1$ degeneracy is used to assign the value of J to all the calculated levels for the linear species and the lowest 4 values of J for the T-shaped

Figure 4: Rotational partition functions for the two conformers of the HeBr_2 as a function of temperature. Solid lines are calculated from the MCTDH results and dashed lines from the rigid rotor model.

Figure 5: Relative partition functions for the linear and T-shaped isomers of the HeBr_2 as a function of the temperature from the MCTDH and RR calculations.

Figure 6: Crossing point temperature T_C as a function of the relative binding energies ΔE of the two HeBr₂ isomers for both MCTDH and RR data.

species. These states are within 7 cm^{-1} ($\sim 10 \text{ K}$) above the energy of the ground linear level, and have found to exhibit a clear rigid rotor behavior for both conformers.

A simple thermodynamical model,²² based on Boltzmann distributions is implemented to investigate the populations of linear and T-shaped HeBr₂ isomers. The model assumes that the two populations are in thermal equilibrium. We found that the ratio of T-shaped to linear complex populations is increasing as the temperature increases, and we observed the population conversion from the linear to T-shaped complexes at temperature value of $T_C=2.87 \text{ K}$ on the basis of the MCTDH calculations. The high sensitivity of this critical temperature to the binding energy difference ΔE was shown by calculating T_C with the experimental value of $\Delta E=0.4 \text{ cm}^{-1}$, that provides a lower value of $T_C=1.60 \text{ K}$. Thus, it may be also useful to record spectra of the HeBr₂ complex at various downstream distances, and thus different temperature regimes, in order to determine the preferential stabilization of the isomers by changing the temperature.

The results presented here were obtained from a full dimensional quantum mechanical treatment that allows a space fixed description of triatomic molecules in Jacobi coordinates. Thus, this

study provides the methodology to treat these molecules embedded in different environments. In particular, this methodology could serve in studying doped helium nanodroplets or intermediate-sized doped helium clusters,^{31–35} where triatomic molecules embedded in a fixed framework can be considered as intermediate steps. Such investigations would require the full description of the rotational degrees of freedom and, in these sense, the present study could provide a benchmark calculation to such future studies of triatomic molecules that need to be fully referred to its environment. Our future efforts should involve the treatment of the high dimensional potential energy surfaces needed to describe this kind of systems and the extension of this methodology to triatomic bent molecules.^{6,36–38}

Acknowledgement

The authors thank to Centro de Calculo del IFF, and SGAI (CSIC) for allocation of computer time. This work has been supported by MINECO grant No. FIS2014-51933-P, COST Actions CM1204 (XLIC) and CM1405(MOLIM), and by the Research Headquarters Address Bogota - DIEB, National University of Colombia.

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