He⁷⁹Br₂ $B, v=8 \leftarrow X, v''=0$ excitation spectrum: *Ab initio* prediction and spectroscopic manifestation of a linear isomer

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The $B \leftarrow X$ rovibronic excitation spectrum of the HeBr₂ van der Waals complex is calculated using an *ab initio* potential energy surface for the ground electronic state. The coupled-cluster single double triple calculations predict double-minimum topology (linear and T-shaped wells) for the X-state potential with a low isomerization barrier. The two lowest vibrational levels, assigned to T-shaped and linear isomers using the localization patterns of the corresponding wave functions, are almost degenerated and lie slightly above the isomerization barrier. This indicates that T-shaped and linear isomers can coexist even at low temperatures and give rise to two separated bands in the excitation spectrum. The main band of the $B \leftarrow X$ excitation spectrum is assigned to transitions from the T-shaped isomer, whereas the very good agreement between the observed and calculated spectrum, using the *ab initio* X-state potential, demonstrates that the unassigned secondary band corresponds to excitation of the linear isomer of the HeBr₂(X) complex. The complete assignment of the spectrum in terms of individual rovibronic transitions is presented. © 2002 American Institute of Physics. [DOI: 10.1063/1.1502638]

I. INTRODUCTION

Recent studies on the intermolecular interactions in van der Waals (vdW) complexes formed by a rare gas atom and an halogen molecule have shown that these systems are not so simple as might be expected.¹ *Ab initio* electronic structure calculations (reviewed in Ref. 1) and some semiempirical models^{2–4} have predicted the existence of a linear isomer on the ground-state surface of such complexes; it is of great interest to know how these linear isomers can be detected experimentally. Klemperer and co-workers^{5,6} have presented clear evidence for the existence of a linear ArI₂(X) isomer via continuous absorption and emission spectroscopy, finding which has been supported by theoretical calculations.^{7,8} Recently, Heaven and co-workers have assigned some vibrational features of the NeI₂(X) excitation and action spectra to the linear isomer.⁹ However, a detailed test of the theoretical predictions about the linear isomer requires us to demonstrate its manifestation in the spectra of lighter complexes, where at least partial resolution of rotational structure is possible.

The $B, v=8 \leftarrow X, v''=0$ excitation spectrum of the HeBr₂ complex (here v and v'' refer to the vibrational excitation of the Br₂ subunit) observed by Janda and co-workers¹⁰ consists of two bands. The main one, shifted by 3.72 cm⁻¹ to the blue from the corresponding band of the bare Br₂ molecule, has a structure typical for transitions from a T-shaped isomer. The secondary band, shifted by 5–6 cm⁻¹ further to the blue, has a complicated structure and an

intensity approximately five times lower than the main band. In a previous paper,¹¹ we have suggested that the secondary band is related to the excitation of the linear isomer. Using a family of model ground-state potentials with variable well depths for the two isomers, we have analyzed the variation of the excitation spectrum and confirmed that the measured spectrum likely corresponds to a situation of two almost degenerated (within half a wave number) ground vibrational levels of T-shaped and linear isomers. However, the model potential of the X state has not allowed us to reproduce quantitatively the partially resolved rotational structure of the spectrum. Therefore, we present new simulations of the HeBr₂ excitation spectrum, performed using an accurate *ab initio* ground-state potential energy surface (PES).¹² It has been found that the coupled-cluster single double triple (CCSD(T)) PES provides a quantitative agreement with available experimental data on the structure and energetics of the HeBr₂(X) complex. Therefore, it is expected that the theoretical simulation of the excitation spectroscopy using the CCSD(T) PES will prove the assignment of the experimental spectrum.¹⁰

II. THEORETICAL METHODS

A. *Ab initio* calculations

The *ab initio* data were calculated at the CCSD(T) level of theory using for bromine atoms the Stuttgart group (SDD) effective core potential incorporated in the GAUSSIAN 98 programs,¹³ augmented with (*sp*) diffusion and (*3df*) polarization functions, SDD+G(*3df*).¹⁴ For the He atom we used augmented correlation consistent aug-cc-pV5Z basis sets supplemented with an additional set (*3s3p2d2f1g*) of bond functions.¹⁵

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We used Jacobi coordinates (r, R, θ) to describe the triatomic HeBr_2 complex, where R is the intermolecular distance of He atom from the center-of-mass of Br_2 , r is the bond length of Br_2 , and θ is the angle between the $\mathbf{R}$ and $\mathbf{r}$ vectors. Several intermolecular distances R from 2.5 to 10 Å were examined and, for each of them, calculations were performed at four angles θ equally spaced in the $(0, \pi/2)$ interval, with r fixed at the equilibrium value of 2.28 Å. For each θ , analytical Morse–vdW-type forms have been used to fit the CCSD(T) interaction energies with parameters given in Ref. 12. The angular dependence of the potential surface was represented using an expansion in Legendre polynomials,

$$V(R, \theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos \theta) \quad (1)$$

with $\lambda = 0, 2, 4, 6$. The accuracy of the $V(R, \theta)$ potential is tested by comparing with additional *ab initio* points calculated at a fifth angle ($\theta = 45^\circ$). It is found that there is a maximum deviation of 2 cm^{-1} and a standard deviation of 0.8 cm^{-1} between the model $V(R, \theta)$ [Eq. (1)] potential and the additional computed *ab initio* points. Thus, the expansion of Eq. (1) up to $\lambda = 6$ was considered enough for the purpose of the present calculations.

B. Spectral simulations

The B state is described¹¹ by a semiempirical analytical PES obtained using the first-order intermolecular diatomics-in-molecule perturbation theory approach (see Ref. 16 and references therein). This PES has global minimum for the T-shaped configuration and a very shallow secondary minimum at the linear configuration.

The procedure for spectral simulations is described in Ref. 11. The bound levels of the $\text{HeBr}_2(X)$ complex are calculated by solving the two-dimensional variational problem for each rotational symmetry block $J''_{p_i p_j}$ defined by the value of the total rotational angular momentum J'' , total parity p_i'' , and parity associated with inversion of Br nuclei p_j'' . The levels of the excited $\text{HeBr}_2(B, v=8)$ complex, metastable with respect to vibrational predissociation, are approximated by the bound levels within a diabatic decoupling approximation.¹¹ The corresponding eigenenergies and eigenfunctions are obtained by solving the two-dimensional variational problem for the total nuclear Hamiltonian averaged over Br_2 internuclear distance using the $\text{Br}_2(B, v=8)$ vibrational wave function. Intensities of dipole allowed $J_{p_i p_j} \leftarrow J''_{p_i p_j}$ transitions [$J = J'', J'' \pm 1$ ($0 \nleftrightarrow 0$); $p_i = -p_i''$; $p_j = -p_j''$] are calculated, under the Franck–Condon approximation, as the squared transition dipole moment matrix elements. Transitions between up to seven lowest van der Waals bound levels of the X and B states (n_X, n_B) in each symmetry block for $J'' \leq 6$ are considered. The resulting stick spectrum is dressed by Lorentzian functions of widths reflecting their vibrational predissociation of the $\text{HeBr}_2(B, v=8)$ complex, and summed up with Boltzmann weights corresponding to a given internal temperature. The total spec-

FIG. 1. The HeBr_2 $B, v=8 \leftarrow X, v''=0$ excitation spectrum. (Top panel) Experiment (see Ref. 10) (bottom panel) best simulations obtained with the model X -state PES (see Ref. 11) and (middle panel) present simulations obtained with *ab initio* X -state PES. The blueshift with respect to the $\text{Br}_2 \times B, v=8 \leftarrow X, v''=0$ transition is taken as abscissa.

trum is composed of more than 3000 individual rovibronic transitions and the calculated transition frequencies are available in an EPAPS document.¹⁷

III. RESULTS

The X -state CCSD(T) PES has two minima in linear and T-shaped configurations with equilibrium distances R_e and well depths (R_e, D_e) of (4.42 Å, 48.8 cm^{-1}) and (3.58 Å, 40.3 cm^{-1}), respectively. While *ab initio* calculations predict a deeper well in the linear configuration, the ground vibrational vdW level $n_X=0$ of the $\text{HeBr}_2(X)$ complex corresponds mainly to the T-shaped isomer. Huang *et al.* have also found¹⁸ a higher zero-point vibrational energy for the linear configuration than the T-shaped one in the HeCl_2 case. The second lowest vdW vibrational level $n_X=1$ is localized mainly in the linear well, and lies only $\sim 0.5 \text{ cm}^{-1}$ higher than the ground one. This finding is in accord with the prediction of the X -state model potential used before.¹¹ For $J''=0$, the two lowest vdW levels, which correspond to the T-shaped and linear isomers, are found at the energies of -17.7 and -17.2 cm^{-1} , respectively, with respect to the $\text{He}+\text{Br}_2$ dissociation limit. It is interesting to note that both vdW levels lie slightly above the isomerization barrier (at energy $\sim -18 \text{ cm}^{-1}$), while the corresponding wave functions are localized mainly at the T-shaped and linear wells, with tunneling through the barrier.

The HeBr_2 $B, v=8 \leftarrow X, v''=0$ excitation spectrum was first simulated using the same conditions as in Ref. 11,

FIG. 2. The main band of the HeBr₂ $B, v=8 \leftarrow X, v''=0$ excitation spectrum: (solid line) experiment (see Ref. 10), (dashed line) simulations shifted by 0.27 cm^{-1} to the red.

namely, at the internal temperature of 1.6 K^{19} and using an average half width of 0.023 cm^{-1} for all the transitions. In Fig. 1, three spectra are presented. The top one is the experimental, the bottom one represents the best result of the simulations using the model X -state potential,¹¹ and the middle one is obtained using the *ab initio* X -state PES. Compared to the experimental spectrum, the one obtained in the present work is slightly blueshifted (by $\sim 0.3 \text{ cm}^{-1}$) and underestimates the intensity of the secondary band. However, its structure agrees with the experimental data much better than the spectrum obtained with the model X -state potential. The present results allow us to analyze sensitivity and structure of the simulated spectra in more detail. We check the assumption of a single linewidth for all the transitions. In the new calculations the half widths of the transitions to the lowest $n_B=0-3$ levels are taken from Fermi Golden rule calculations on the vibrational predissociation at $J=0$ (0.013 , 0.032 , 0.023 , and 0.020 cm^{-1} , respectively). For the upper levels $n_B>3$ which appear at higher J values, the half width for the $n_B=3$ level is used. It is found that the spectrum is almost insensitive to the variation of the linewidths. The reason is twofold: (i) the individual widths are not very different; and (ii) the peaks are composed from a number of rotational transitions so the resulting profile is more sensitive to their spacing rather than to the broadening. Therefore, further refinement of the linewidth parameters was not accounted for. Also, the dependence of the spectrum on the internal temperature is analyzed. The overall intensity of the secondary band increases with temperature only slightly, while the red wing of the main band depends strongly on temperature. Using a rotational temperature of 2.2 K (instead of 1.6 K) a better agreement with experimental data is achieved. Thus, the discussion below concentrates only on the results of the simulations at this temperature.

Measured and simulated profiles of the main band are shown in Fig. 2 (the latter is corrected by a shift of 0.27 cm^{-1} to the red), showing a remarkable agreement. In Fig. 3 the simulated profile is superimposed by sticks representing

FIG. 3. The main band of the simulated HeBr₂ $B, v=8 \leftarrow X, v''=0$ excitation spectrum superimposed by the stick spectrum of the dominant rovibronic transitions. Assignment legends are $n_X, J''p_i''p_j''/n_B, Jp_i p_j$.

around 300 individual rovibronic transitions whose intensity exceeds 0.5% of the maximum. The assignment of the dominant sticks is made in terms of vibrational and rotational quantum numbers $n_X, J''p_i''p_j''/n_B, Jp_i p_j$. It clearly shows that the main band is composed by various $n_X=0 \rightarrow n_B=0$ transitions between T-shaped isomers of the complex with a small admixture of $n_X=0 \rightarrow n_B=1$ and $n_X=1 \rightarrow n_B=0,1$ transitions, where the latter two correspond to the linear ground state isomer. These secondary transitions perturb the structure of the main band which can be described using an asymmetric top model and may be detected in high-resolution spectra.

The results for the secondary band are presented in Fig. 4 (simulated spectrum is corrected by a shift of 0.32 cm^{-1} to the red and multiplied by 3.9). Despite some minor (less than 0.1 cm^{-1}) deviations in the peak positions, mainly at the far blue wing of the spectrum, and somewhat different intensity distribution among the peaks, the structures of the simulated spectrum lines are in almost one-to-one correspondence with the observed ones. This enables the assignment of the spectrum. Because many individual rovibronic transitions contribute to the spectrum with similar intensities, the assignment is made by simulating the spectrum profiles for each vibronic $n_X \rightarrow n_B$ transition as shown in Fig. 4 for the dominant peaks, instead of analyzing the stick spectrum. In cases of strong mixing, the contributing transitions are listed in descending order. The main contribution to the secondary band is due to transitions from the linear isomer $n_X=1$ to the