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Structure and spectroscopy of the He_2Cl_2 van der Waals cluster

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The rovibrational structure of the He_2Cl_2 van der Waals cluster in the X and B electronic states is studied by means of full dimensional quantum-mechanical calculations. He_2Cl_2 is the smallest cluster containing helium for which rotationally state-resolved data are available and for which the effects of Bose statistics are important. The He_2Cl_2 wave functions exhibit quite large amplitude motions, particularly for the He–He bending mode [associated with the angle formed between the two He–(center of mass of Cl_2) bonds]. The preferred geometry of the ground van der Waals state is planar, with the He–He axis perpendicular to the Cl_2 axis. It is shown that a reduced dimension model for the He–He bending vibration together with a rigid structural model reproduces well the low-lying energy levels of the complex and allows us to assign proper statistical weights to the asymmetric top transitions of the $B \leftarrow X$ spectra. In particular, the symmetry under He exchange of the rigid rotor levels is shown to depend on the He–He bending level. The observed excitation spectra are successfully simulated using the proposed model. The effective rigid structure that best reproduces the rotationally excited levels with a rigid rotor analysis is a distorted tetrahedron where the He–He angle is approximately 130° . This difference from the 180° most probable configuration is due to the complex dependence of the moments of inertia on the internal degrees of freedom for such a floppy molecule. Therefore, structural information obtained from observed spectra of this or similar clusters should be carefully analyzed to avoid reaching misleading conclusions. Fragmentation rates for $\text{He}_2\text{Cl}_2(B, v=10-13)$ are, for the first time, extracted from experimental data, confirming that the dissociation process is mainly sequential. © 2000 American Institute of Physics. [S0021-9606(00)02141-3]

I. INTRODUCTION

Since the laser excited fluorescence spectrum of HeI_2 was first reported by Levy and co-workers,¹ intense experimental as well as theoretical work has been devoted to the study of the spectroscopy and predissociation dynamics of van der Waals clusters consisting of a halogen molecule and several rare gas atoms. The most recent advances and current frontiers in this field have been reviewed recently.² Various interesting aspects like coupled large amplitude vibrations, pairwise interactions versus many-body effects, intramolecular vibrational redistribution, and the size evolution of static and dynamic properties of these clusters have been studied over the last several years. Also, recent experiments and theoretical simulations have started to explore the behavior of molecules interacting with helium from the large cluster limit.^{3,4} Among the attractive properties of large helium clusters are a very low temperature, 0.4 K, and the very weak interaction between the helium and the guest molecules. These properties may make large helium clusters a nearly ideal “matrix” for studying molecular structure and dynamics of complex species. Concomitantly, studying the behav-

ior of guest molecules in the large helium clusters will give new insight into the unusual properties of superfluidity in mesoscopic systems. Among the results obtained so far are the coupling of the electronic excitations of glyoxal to the roton modes⁵ of the superfluid helium and the contrast between the rotational behavior of OCS in clusters of ^4He and ^3He .⁶ In ^4He , OCS behaves as a free rotor, except that the rotational constant is smaller than that of the free molecule. In ^3He , an unstructured spectrum is observed as though the OCS rotation were completely quenched. ^4He was gradually added to ^3He to determine that the coherent rotational motion of OCS is restored upon the addition of 60 ^4He atoms. It is interesting to note that the velocity of the oxygen atom in a $J=4$ rotating OCS molecule is of the order of 40 m/s, near the critical velocity of superfluid helium. The change of the rotational constant of a molecule upon insertion into the ^4He environment has been first interpreted as being due to the “rigid” attachment of several helium atoms (of the non-superfluid component) to the guest molecule,⁷⁻¹⁰ like a van der Waals complex. The van der Waals complex was then considered to be rotating freely in the superfluid environ-

ment. More recently, a quite different interpretation for the increase of the moment of inertia has been given, based on a superfluid hydrodynamical model and assuming a spatially inhomogeneous superfluid.¹¹ We hope that our current study of the interaction of helium with chlorine for the case of two helium atoms may be a step toward bridging the gap between the small cluster and the large cluster limit. Although we will show that the two helium atoms are quite delocalized on a “ring” around the center of the Cl_2 molecular axis, the analysis of the spectrum of the molecule in terms of a rigid structure is surprisingly effective.

Sands, Bieler, and Janda¹² were the first to obtain rotationally resolved spectra of a complex containing more than one helium atom. The complex in its ground state (X, v'') is excited to a quasibound state correlating with the (B, v) state of Cl_2 . After several vibrational periods the cluster fragments, leaving Cl_2 in specific rovibrational states of the B electronic state. Difficulties in the fit of the observed excitation spectra by means of rigid rotor analysis were initially attributed to extremely wide amplitude motions of the He atoms within the cluster. Although not surprising, this result contrasted with the remarkable success of simple structural models on similar clusters with heavier rare gas atoms, like Ne_2Cl_2 ¹³ and Ar_2Cl_2 .¹⁴ In a quantum Monte Carlo study¹⁵ of the ground state of this cluster, it was indeed found that He_2Cl_2 is an exceptionally fluxional van der Waals complex, although the rare gas atoms tend to localize on a ring about the diatomic due to the anisotropy of the He– Cl_2 interaction. Similar conclusions were reached by García-Rizo *et al.*,¹⁶ where diffusion Monte Carlo calculations were performed for calculating $\text{He}_2\text{Cl}_2(B, v)$ quasibound states of the excited electronic state by means of a diabatic approximation. Villarreal *et al.*,¹⁷ performed full dimensional variational calculations of He_2Cl_2 energy levels at zero total angular momentum, $J=0$. In addition to the mentioned structure of the ground van der Waals state, they found that the first excited van der Waals level, which is related to a bending motion [associated with the pseudotriatomic He–(center of mass of Cl_2)–He bending angle], has a frequency of the same order of magnitude as the rotational constants of the whole system. A large coupling between this vibrational mode and the rotational modes would be the origin of the failure of the rigid rotor model. McMahon and Whaley¹⁸ found, by means of quantum Monte Carlo computations, that the ground-state ring structure is preserved in the He_6Cl_2 cluster. More recent calculations by Lewerenz¹⁹ show that He density begins to grow above and below Cl_2 for He_8Cl_2 .

Hernández and Halberstadt²⁰ (hereafter referred to as Paper I) performed full dimensional quantum-mechanical calculations of $J \geq 0$ energy levels of He_2Cl_2 and excitation spectra for the ($B, v=8$) $\leftarrow$ ($X, v''=0$) transition. An excellent agreement was found with the measured spectra of Sands *et al.*¹² The first excited van der Waals level ($v=1$) was found to lie $\approx 0.5 \text{ cm}^{-1}$ above the ground van der Waals state ($v=0$), so transitions involving the former also contribute to the spectra at typical temperatures ($\approx 1 \text{ K}$). Surprisingly, although such a frequency is of the same order of magnitude as the system rotational constants (≈ 0.1 – 0.2 cm^{-1}), it was found that using a simple asymmetric top

Hamiltonian (where the rotational constants depend on the vibrational state), the full dimensional rotationally excited states are reproduced quite accurately. The initial difficulties for performing direct fits to measured spectra using rigid rotor models were then explained as a combination of two effects. First, the non-negligible contributions to the spectra of the low-lying excited van der Waals states. More importantly, in order to assign statistical weights, the behavior of the rigid rotor states under He or Cl permutations (He and Cl nuclear spins are zero and $3/2$, respectively), has to be determined, and it depends on the van der Waals He–He bending level. This problem is crucial for He, as the antisymmetric states have zero statistical weight, so half the rotational levels are missing.

In this paper we perform a more detailed analysis of the rovibrational structure of the He_2Cl_2 cluster. There are two main goals of this work. First, to explore the relationship between the averaged geometry of the cluster and the energy level structure of the rotationally excited states, by computing wave function probability distributions as functions of the internal degrees of freedom and expectation values of rotational constants. A contradictory result that will be explained is that the rigid rotor analysis performed in Paper I indicates that the ground-state molecular geometry is that of a distorted tetrahedron with a He–He angle of about 135° , while the analysis of the $J=0$ wave function performed by Villarreal *et al.*¹⁷ suggests that the cluster geometry is planar (a He–He angle of 180°). Second, we will provide a simple procedure to effectively use the rigid rotor model as a tool to extract structural and dynamical information from observed spectra of this and similar complexes. We show here that by combining the rigid rotor model with a reduced dimensional model for the He–He bending mode, not only can the energy levels be successfully reproduced, but also the behavior of the rovibrational states under the permutation-inversion operations is correctly predicted. The comparison with the observed ($B, v=8$) $\leftarrow$ ($X, v''=0$) spectrum using this simplified model is found to be successful.

Sands *et al.*¹² have measured the rotationally resolved spectra of $\text{He}_2\text{Cl}_2(B, v)$ for $v=10$ – 13 . Here, by fitting model parameters to experimental data, homogeneous linewidths [due to the fragmentation rates of the $\text{He}_2\text{Cl}_2(B, v)$ quasibound states] are extracted for $v=10$ – 13 . These are the first experimentally based estimations of this dynamical information, since linewidths could not previously be obtained from the data because the rigid rotor model provided a poor fit. The He_2Cl_2 fragmentation dynamics is also an interesting subject. Sands *et al.*¹² obtained vibrational and rotational distributions of the Cl_2 fragment and found that the loss of two quanta dominates the predissociation dynamics of the complex (even though there is enough energy to leave the fragment in the $v-1$ state). This suggests that the main fragmentation pathway is sequential

as the Cl_2 must lose at least one quantum in each dissociation step, the final fragment must be found in a vibrational state $v_f \leq v-2$. This sequential character was recently used in a theoretical study of the vibrational predissociation of He_2Cl_2

in which departure of the first helium atom was described classically, and the second one quantum mechanically.²¹ The classical part of the simulation provided the state distribution of the HeCl_2 intermediate, which was used to average over the final state distribution obtained in the quantum-mechanical part. The resulting Cl_2 rovibrational state distributions were found in very good agreement with the experimental ones.

However, Sands *et al.*¹² also found a non-negligible population corresponding to the $v-1$ channel (a population of 8% was found for $v=8$). This would involve a competing direct fragmentation process

Another possibility would be the formation of He_2 , but this process appears to be very unlikely. Extraction of the decay rates from the linewidths of the experimental data indicates that the He_2Cl_2 rates are slightly larger than twice the HeCl_2 (as initial parent molecule) dissociation rates, suggesting that the process is mainly sequential but that either the departure of the first He atom is somewhat affected by the second He or that the direct process, Eq. (1.2), speeds up the overall rate slightly.

The paper is organized as follows. In Sec. II the full dimensional quantum-mechanical treatment to obtain rovibrational states of the cluster is presented. Section III is divided into four parts. First, the full dimensional $J=0$ energy levels and probability distributions are reported and are compared with those obtained by a reduced dimension model for the He–He bending. Second, the full dimensional $J>0$ energy levels and permutation-inversion symmetry labels are given and compared with those corresponding to rigid rotor models. Third, it is shown, using information from the reduced dimension He–He bending model, that the behavior of the rigid rotor states under the permutation-inversion operators can be determined, so that statistical weights of spectrum transitions can be properly given. And fourth, this combined model is used to fit the observed spectra and extract lifetimes for the states. Finally, some concluding remarks are given in Sec. IV.

II. THEORY

A. Potential energy surface

It is assumed that Cl–Cl, He– Cl_2 , and He–He interactions contribute independently to the potential energy surface. Potential energy functions for the He– Cl_2 interaction in electronic states X and B were taken from Ref. 22, where it is shown that such functions describe very well scattering, spectroscopy and vibrational predissociation data of the triatomic complex. $V_{\text{Cl-Cl}}(X,B)$ interaction potentials were taken from Ref. 23, where Rydberg–Klein–Rees (RKR) potentials are extracted from spectroscopic data. For the He–He interaction (which is assumed to be identical for both electronic states X and B), we used the semiempirical potential proposed by Aziz and Slaman in Ref. 24. This potential is consistent with several types of experimental data and also with *ab initio* calculations for the ground electronic state of He_2 . In view of the excellent comparison with the measured

spectra achieved in Paper I, where the same potential energy surface was used, we believe that this surface is useful for calculating the He_2Cl_2 . It should be noted that much work has been devoted recently to construct improved He– Cl_2 potential energy surfaces based on *ab initio* points as well as sophisticated multiproperty fits.^{25–29} These surfaces are similar around the perpendicular well and differ around the collinear configuration which is found to be a deeper potential minimum (for the X state) in the more accurate surfaces. However, because of zero-point energy, the corresponding quantum state is ca. 1.7 cm^{-1} higher in energy than the perpendicular state.³⁰

B. Full dimensional quantum-mechanical calculations

Valence coordinates are used to describe the nuclear motion of the He_2Cl_2 system. After separation of the center of mass motion, the remaining nine degrees of freedom are given by $\underline{r}$, the vector joining the two chlorine nuclei, and $\underline{R}_1$ and $\underline{R}_2$, the vectors pointing to the two helium atoms, having their common origin in the center of mass of Cl_2 . These coordinates are convenient due to the small ratio between the helium and chlorine masses and the slight interaction between the two helium atoms. A body-fixed frame is chosen so that its z component is along the $\underline{r}$ vector. Thus, the polar angles of $\underline{r}$, denoted as θ_r and ϕ_r , specify the orientation of $\underline{r}$ in the laboratory frame, while (θ_1, ϕ_1) and (θ_2, ϕ_2) describe the orientation of $\underline{R}_1$ and $\underline{R}_2$, respectively, with respect to the body-fixed frame. Throughout the paper we will refer to the present approach as full dimensional calculations.

The Schrödinger equation is written in these coordinates as

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{j^2}{2\mu r^2} + V_{\text{Cl}_2}(r) + \sum_{i=1,2} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R_i^2} + \frac{l_i^2}{2m R_i^2} \right) + V_{\text{Cl}_2-\text{He}}(r, R_i, \theta_i) + V_{\text{He-He}}(\underline{R}_1, \underline{R}_2) - \frac{\hbar^2}{2M_{\text{Cl}}} K_{R_1 R_2} \right] \times \Psi(\underline{r}, \underline{R}_1, \underline{R}_2) = E \Psi(\underline{r}, \underline{R}_1, \underline{R}_2), \quad (2.1)$$

where the total wave function has been written as $\Psi' = \Psi/(rR_1R_2)$ and the reduced masses are $\mu = M_{\text{Cl}}/2$ and $m = M_{\text{He}}M_{\text{Cl}_2}/(M_{\text{He}} + M_{\text{Cl}_2})$. In Eq. (2.1), j , l_1 , and l_2 are the angular momenta associated with $\underline{r}$, $\underline{R}_1$, and $\underline{R}_2$, respectively. $K_{R_1 R_2}$ is a crossing kinetic term, which is expected to become important only when very high angular excitations are involved.¹⁷ Since we are dealing with the lowest energy levels, and taking into account the relatively high mass of chlorine, this term has been neglected in the present treatment. In addition, the Cl_2 vibration is decoupled from the other degrees of freedom, taking into account the large frequency difference between such a mode and the van der Waals modes. Within this (adiabatic) approximation, the total wave function is given by

$$\Psi_v^0(\underline{r}, \underline{R}_1, \underline{R}_2) = \chi_v(r) \hat{\Psi}^v(\hat{r}, \underline{R}_1, \underline{R}_2), \quad (2.2)$$

where χ_v is the ($X, v=0$) or (B, v) vibrational wave function of Cl₂. The Schrödinger equation [Eq. (2.1)] is premultiplied by $\langle \chi_v |$ and integration is performed on r , with the result

$$\left[\epsilon_v + \frac{B_v j^2}{\hbar^2} + \sum_{i=1,2} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R_i^2} + \frac{l_i^2}{2mR_i^2} + V_{\text{Cl}_2-\text{He}}^v(R_i, \theta_i) \right) + V_{\text{He-He}}(\underline{R}_1, \underline{R}_2) \right] \hat{\Psi}^v = E \hat{\Psi}^v, \quad (2.3)$$

where ϵ_v is the Cl₂ vibrational energy, $V_{\text{Cl}_2-\text{He}}^v(R_i, \theta_i) = \langle \chi_v | V_{\text{Cl}_2-\text{He}}(r, R_i, \theta_i) | \chi_v \rangle$, and $B_v = \langle \chi_v | \hbar^2 / (2\mu r^2) | \chi_v \rangle$. The orthonormal basis set used to solve Eq. (2.3) is given by

$$\begin{aligned} & \Phi_{(\Omega_1 n_1 \lambda_1)(\Omega_2 n_2 \lambda_2)}^{JM\Omega}(\underline{r}, \underline{R}_1, \underline{R}_2) \\ &= \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{M\Omega}^{J*}(\phi_r, \theta_r, 0) \psi_{(\Omega_1 n_1 \lambda_1)}(\underline{R}_1) \\ & \quad \times \psi_{(\Omega_2 n_2 \lambda_2)}(\underline{R}_2), \end{aligned} \quad (2.4)$$

with the condition

$$\Omega_1 + \Omega_2 = \Omega. \quad (2.5)$$

In Eq. (2.4), $D_{M\Omega}^J$ are Wigner functions depending on the orientation of the $\underline{r}$ vector, J is the quantum number associated with the total angular momentum $\underline{J} = \underline{j} + \underline{l}_1 + \underline{l}_2$, M and Ω are quantum numbers associated with the projection of $\underline{J}$ on the laboratory Z axis and the body-fixed z axis, respectively, and Ω_1 and Ω_2 are quantum numbers associated with the projections of $\underline{l}_1$ and $\underline{l}_2$ on the body-fixed z axis. Finally, $\psi_{(\Omega_i n_i \lambda_i)}(\underline{R}_i)$ is an eigenfunction of

$$H_{\text{Cl}_2-\text{He}}^v = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R_i^2} + \frac{l_i^2}{2mR_i^2} + V_{\text{Cl}_2-\text{He}}^v(R_i, \theta_i). \quad (2.6)$$

As can be seen, we are employing a “configuration-interaction” method,³¹ where the configurations are built as products of the wave functions of $H_{\text{Cl}_2-\text{He}}^v$, which is the Hamiltonian of HeCl₂ except for the term $\epsilon_v + B_v j^2$. These HeCl₂ wave functions are expanded as

$$\psi_{(\Omega_i n_i \lambda_i)}(\underline{R}_i) = \sum_{d_i l_i} c_{d_i l_i}^{(\Omega_i n_i \lambda_i)} \phi_{d_i}(\underline{R}_i) Y_{l_i \Omega_i}(\theta_i, \phi_i), \quad (2.7)$$

where $Y_{l_i \Omega_i}$ are spherical harmonics and ϕ_{d_i} are harmonic oscillator functions. Furthermore, λ_i is an index related to the chlorine exchange symmetry. Since Cl₂ is homonuclear, the van der Waals potential is symmetric under the operation $\theta_i \rightarrow \pi - \theta_i$ and therefore, $\psi_{(\Omega_i n_i \lambda_i)}(\underline{R}_i)$ are given as linear combinations of spherical harmonics with l_i even or odd. Thus, λ_i indicates the parity of the l_i 's. Finally, n_i labels the vibrational van der Waals excitation.

We have considered the following symmetry operations. First, the inversion of all the nuclear coordinates ($\underline{r} \rightarrow -\underline{r}, \underline{R}_1 \rightarrow -\underline{R}_1, \underline{R}_2 \rightarrow -\underline{R}_2$), second, the exchange of chlorine atoms ($\underline{r} \rightarrow -\underline{r}$), and third, the exchange of helium atoms ($\underline{R}_1 \rightarrow \underline{R}_2, \underline{R}_2 \rightarrow \underline{R}_1$). In Table I the effects of the correspond-

TABLE I. Effect of the symmetry operators on a primitive basis function $\Phi_{(\Omega_1 n_1 \lambda_1)(\Omega_2 n_2 \lambda_2)}^{JM\Omega}$.

Inversion	$(-1)^J \Phi_{(-\Omega_1 n_1 \lambda_1)(-\Omega_2 n_2 \lambda_2)}^{JM-\Omega}$
Cl-Cl exchange	$(-1)^J \lambda_1 \lambda_2 \Phi_{(-\Omega_1 n_1 \lambda_1)(-\Omega_2 n_2 \lambda_2)}^{JM-\Omega}$
He-He exchange	$\Phi_{(\Omega_2 n_2 \lambda_2)(\Omega_1 n_1 \lambda_1)}^{JM\Omega}$

ing operators on the basis functions are summarized. Taking into account the results given in that table, a new symmetry-adapted basis set is built

$$\begin{aligned} & \Theta_{(\Omega_1 n_1 \lambda_1)(\Omega_2 n_2 \lambda_2)}^{JM\bar{\Omega}\epsilon\kappa\eta} \\ &= N \{ \Phi_{(\Omega_1 n_1 \lambda_1)(\Omega_2 n_2 \lambda_2)}^{JM\bar{\Omega}} + \epsilon(-1)^J \Phi_{(-\Omega_1 n_1 \lambda_1)(-\Omega_2 n_2 \lambda_2)}^{JM-\bar{\Omega}} \\ & \quad + \kappa \Phi_{(\Omega_2 n_2 \lambda_2)(\Omega_1 n_1 \lambda_1)}^{JM\bar{\Omega}} \\ & \quad + \kappa \epsilon(-1)^J \Phi_{(-\Omega_2 n_2 \lambda_2)(-\Omega_1 n_1 \lambda_1)}^{JM-\bar{\Omega}} \}, \end{aligned} \quad (2.8)$$

where N is a normalization factor and $\bar{\Omega} = |\Omega|$. The functions given by Eq. (2.8) are eigenfunctions of the inversion, helium exchange, and chlorine exchange operators, with eigenvalues ϵ , κ , and $\eta = \epsilon \lambda_1 \lambda_2$, respectively, their possible values being $+1$ or -1 . Equation (2.3) is solved for each value of J , for the eight symmetry blocks [all the combinations of (ϵ, κ, η)].

C. Computational details

Triatomic wave functions [Eq. (2.7)] were computed using an angular basis of 14 spherical harmonics and a radial basis of 19 harmonic oscillator functions with an equilibrium position $R_e = 5.5 \text{ \AA}$ and frequency $\omega = 16 \text{ cm}^{-1}$. An equivalent radial discrete variable representation (DVR) basis (obtained by diagonalizing R in the harmonic oscillator basis) was alternatively employed in order to compute matrix elements of the potential $V_{\text{Cl}_2-\text{He}}^v$. At each DVR point, the potential was expanded in 40 Legendre polynomials depending on the angle θ_i . The diagonalization of the Hamiltonian matrix of Eq. (2.6) was repeated for different values of Ω_i (ranging from 0 to 12) and for $\lambda_i = 1$ (even l_i 's) and $\lambda_i = -1$ (odd l_i 's). For each Ω_i , only the lowest eigenstate ($n_i = 0$) was included in the expansion Eq. (2.4), except for the blocks $[\Omega = 0, 1, \lambda_i = \pm 1]$ and $[\Omega = 2, \lambda_i = +1]$, where $n_i = 1, 2$ states were also included, and the blocks $[\Omega = 3, 4, \lambda_i = +1]$ and $[\Omega = 2, 3, \lambda_i = -1]$, where first excited states ($n_i = 1$) were also selected. In order to solve the tetraatomic eigenvalue problem, matrix elements of $B_v j^2$ and $V_{\text{He-He}}$ are needed [the other terms in Eq. (2.3) are diagonal in the basis of Eq. (2.4)]. The method used to compute the matrix elements of $V_{\text{He-He}}$ is very close to that described in Ref. 17, the only difference coming from the use of the DVR basis. For each combination of $(\underline{R}_1, \underline{R}_2)$ DVR points, the potential was expanded in a series of 60 Legendre polynomials depending on $\cos \gamma$, γ being the angle between the $\underline{R}_1$ and $\underline{R}_2$ vectors. The rest of the procedure, as well as the computation of the matrix elements of $B_v j^2$, was worked out using angular momentum algebra.³² Values for rotational constants were taken from Ref. 23: 0.24325 cm^{-1} and

TABLE II. Energy levels (in cm^{-1}) for He_2Cl_2 for $J=0$ in the indicated vibronic states. $\varepsilon\eta\kappa$ are the eigenvalues under coordinate inversion, Cl_2 exchange, and He_2 exchange, respectively. For the ground van der Waals state ($\nu=0$), the zero of energy is located at the dissociation limit $\text{Cl}_2(X, \nu=0; B, \nu=8) + \text{He} + \text{He}$, while the energies of the excited states are referred to the $\nu=0$ one.

	$\varepsilon\eta\kappa$	$(X, \nu=0)$	$(B, \nu=8)$
$E_{\nu=0}$	+++	-32.173	-25.575
$E_{\nu=1} - E_{\nu=0}$	---	0.532	0.481
$E_{\nu=2} - E_{\nu=0}$	+++	1.458	1.422
$E_{\nu=3} - E_{\nu=0}$	---	3.057	2.895

0.13792 cm^{-1} for the $X(\nu=0)$ and $B(\nu=8)$ states, respectively. For each electronic state, calculations were carried out for total angular momentum $J=0,1,2,3$. After several convergence tests, we estimate that energy levels are converged within 0.1 cm^{-1} . We have not attempted to increase the size of the basis since the computation of expectation values and probability distributions would become too expensive.

III. RESULTS AND DISCUSSION

A. $J=0$ states: Full and reduced dimension calculations

The lowest van der Waals energy levels at zero total angular momentum for He_2Cl_2 in the vibronic states $X(\nu=0)$ and $B(\nu=8)$ are presented in Table II. Note that the second and fourth states of that table are antisymmetric under He-He exchange. These states are forbidden or, in other words, have zero statistical weight. The total wave function must be symmetric under boson exchange, and since the spin wave function is necessarily symmetric due to the zero spin of ^4He nuclei, the rovibrational wave function must always be symmetric. In spite of this, we include the forbidden states in our analysis since this is useful to understand the level structure of the cluster.

Comparing the two sets of energy levels for the X and B states, it can be seen that, although the dissociation energies are rather different, the energy level structure is quite similar in both electronic states. They present an anharmonic level structure, the energy differences between adjacent states being about 0.5, 0.9, and 1.5 cm^{-1} . This suggests that those states are mainly associated with a vibrational He-He mode, weakly coupled with van der Waals He- Cl_2 modes. The He- Cl_2 modes present bending and stretching frequencies which are higher by at least one order of magnitude, and which differ in the X and B states owing to the different He- Cl_2 interaction potentials and the fact that the Cl_2 bond length is larger in the B state. In order to uncover the structure of such states, we have computed their probability densities as functions of the internal coordinates, which are R_i , θ_i ($i=1,2$) and the angle ϕ_- , defined as a linear combination of ϕ_1 and ϕ_2

$$\phi_- = \frac{\phi_1 - \phi_2}{2}, \quad 0 \leq \phi_- \leq \pi. \quad (3.1)$$

Thus, this angle is formed between the projections of the vectors pointing from the center of mass of Cl_2 to the He

FIG. 1. Contour plots of the probability density of the ground van der Waals states of $\text{He}_2\text{Cl}_2(X, \nu=0)$ (upper panel) and $\text{HeCl}_2(X, \nu=0)$ (lower panel) as a function of $x=R \cos \theta$ and $y=R \sin \theta$. Contours are shown at 1.2, 0.6, 0.3, 0.15, and 0.075.

atoms, onto the plane perpendicular to the Cl_2 axis. The vibrational mode related to this angle is hereafter referred to as the “He-He bending mode.” The ϕ_+ angle, defined as

$$\phi_+ = \frac{\phi_1 + \phi_2}{2}, \quad 0 \leq \phi_+ \leq 2\pi, \quad (3.2)$$

is the third Euler angle giving the orientation of the molecule-fixed frame with respect to the space-fixed frame, and thus describes an overall rotation of the system. Once the wave functions are rewritten in these new coordinates, probability densities $\rho_\nu(R_i, \theta_i)$ ($i=1,2$) and $\rho_\nu(\phi_-)$ are obtained by integration of the corresponding modulus of the wave functions over all coordinates except those explicitly indicated.

In the upper panel of Figs. 1 and 2, probability distributions $\rho_\nu(x=R_1 \cos(\theta_1), y=R_1 \sin(\theta_1))$ are presented for the ground state ($J=0, \nu=0$) of the $(X, \nu=0)$ and $(B, \nu=8)$ vibronic states, respectively. The corresponding distributions for the coordinates of the second He atom (R_2, θ_2) are not shown since they are identical. Although probability distributions are quite broad, the He atoms lie on average in a ring perpendicular to the Cl_2 axis. For the sake of comparison, we have computed the ground van der Waals state of the $J=0$ triatomic HeCl_2 complex by diagonalizing the Hamiltonian matrix of $H_{\text{Cl}_2-\text{He}}^\nu$ [Eq. (2.6)] + $\epsilon_\nu + B_\nu j^2$. The corresponding probability distributions as a function of $(x=R \cos(\theta), y=R \sin(\theta))$ are shown in the lower panels of Figs. 1 and 2 for $(X, \nu=0)$ and $(B, \nu=8)$, respectively. The distributions of the tetra-atomic complex are clearly almost identical to the corresponding distributions of the triatomic complex. Hence, the weak He-He interaction scarcely affects the radial and polar distribution of the He atom with respect to Cl_2 . Moreover, the computed triatomic energies are $-16.134[(X, \nu=0)]$ and $-12.838[(B, \nu=8)] \text{ cm}^{-1}$. Doubling these values

FIG. 2. Same as Fig. 1 but for the $(B, v=8)$ vibronic state.

gives energies (-32.268 and -25.676 cm^{-1} for the X and B states, respectively) quite close to the corresponding tetra-atomic ones (-32.173 and -25.575 cm^{-1} , see Table II), indicating that the effective contribution of the He–He interaction is almost negligible. This result was already pointed out by Bačić *et al.*¹⁵ in their quantum Monte Carlo study on the same cluster.

The excited state distributions $\rho_\nu(R_{i=1,2}, \theta_{i=1,2})$, $\nu = 1, 2, 3$ of the tetratomic complex, are found to be almost identical to those already presented for $\nu=0$. Hence, the differences in the ν levels must appear in the $\rho_\nu(\phi_-)$ probability distributions (depicting how the He atoms are distributed over the ring perpendicular to the Cl–Cl axis). These probability distributions are represented in Fig. 3 [for $(X, v=0)$] and Fig. 4 [for $(B, v=8)$]. Note that they are quite similar in the X and B states. It can be seen that the $\nu = 1, 2, 3$ states (for both the X and B electronic states) present clear nodal patterns corresponding to excitations in the He–He bending mode. Also, the ground-state distribution ($\nu=0$) is quite broad, as expected for a floppy mode. It is peaked at $\phi_- = \pi/2$, $\phi_1 - \phi_2 = 180^\circ$, which means that He atoms “prefer” to locate at opposite ends of a vector through the Cl₂ center of mass, perpendicular to the Cl–Cl axis. It is therefore predicted that the most probable geometry of the complex is planar, in accordance with previous calculations within a different treatment and slightly different potential energy surfaces.¹⁷ This geometry substantially differs from that proposed in Paper I ($\phi_2 - \phi_1 = 125^\circ - 150^\circ$), obtained by fitting the rotational energy levels with a rigid rotor model. The origin of this apparent contradiction is discussed in Sec. III B.

The good separation found between the modes associated with the (R_i, θ_i) coordinates and the ϕ_- bending mode suggests that a reduced dimension model for that bending mode should work well and, hopefully, give more insight into the vibrational structure of the cluster. The basis for this model is the diabatic separation between the higher fre-

FIG. 3. (a) Probability density as a function of ϕ_- (in deg), for the ground van der Waals state of He₂Cl₂($X, v=0$), $\nu=0$; (b) Same for the first excited van der Waals state, $\nu=1$; (c) $\nu=2$; (d) $\nu=3$.

quency He–Cl₂ vibrational modes and the He–He vibration and overall rotation: the He–He vibration is solved by using a reduced-dimension Hamiltonian obtained by averaging the full dimension Hamiltonian over all the other vibrational degrees of freedom in their ground, $J=0$ state. The basis function of Eq. (2.4) corresponding to $J=0$, $\Omega=0$, $M=0$, $\Omega_1 = \Omega_2=0$, $n_1=n_2=0$, $\lambda_1=\lambda_2=+$ is given by

$$\Phi_{(00+)(00+)}^{000} = \left(\frac{1}{4\pi}\right)^{1/2} D_{00}^{0*} \psi_{(00+)} \psi_{(00+)} \quad (3.3)$$

Note that this function does not depend on ϕ_r, θ_r (since $D_{00}^{0*}=1$), nor on $\phi_{i=1,2}$, since, taking into account that a spherical harmonic can be written as $Y_{l_i \Omega_i}(\theta_i, \phi_i) = (2\pi)^{-1/2} \Theta_{l_i \Omega_i}(\theta_i) \exp(i\Omega_i \phi_i)$,³² and that $\Omega_i=0$, the corresponding triatomic configurations, are given by

$$\psi_{(00+)}(\underline{R}_i) = (2\pi)^{-1/2} \sum_{d_i l_i} c_{d_i l_i}^{(00+)} \phi_{d_i}(R_i) \Theta_{l_i 0}(\theta_i) \quad (3.4)$$

The total wave function is then written by means of a diabatic separation of (R_i, θ_i) and ϕ_i coordinates

$$\hat{\Psi} = 2\pi \Phi_{(00+)(00+)}^{000} F(\phi_1, \phi_2) \quad (3.5)$$

FIG. 4. Same as Fig. 3 but for the $(B, v=8)$ vibronic state.

Inserting this wave function in Eq. (2.3), multiplying it by $2\pi\Phi_{(00+)(00+)}^{000}$, and integrating over all coordinates except $\phi_{i=1,2}$, we obtain the Schrödinger equation for the reduced dimension model

$$\left[\epsilon_v + B_v \langle j^2 \rangle + 2\epsilon_{00+} + \left\langle \frac{-\hbar^2}{2mR^2} \right\rangle \left[\frac{\partial^2}{\partial \phi_1^2} + \frac{\partial^2}{\partial \phi_2^2} \right] + \langle V_{\text{He-He}}(\phi_1, \phi_2) \rangle \right] F = EF, \quad (3.6)$$

where ϵ_{00+} is the energy of the triatomic configuration $(\psi_{(00+)})$ and $\langle A \rangle = 4\pi^2 \langle \Phi_{(00+)(00+)}^{000} | A | \Phi_{(00+)(00+)}^{000} \rangle$. To obtain Eq. (3.6), note that $\langle -\hbar^2/2mR^2 \rangle = \langle -\hbar^2/2mR_2^2 \rangle$, and the subscript of R has been dropped.

To solve Eq. (3.6), we consider a basis set adapted with respect to the He exchange symmetry

$$\Phi_{\Omega_1\Omega_2\kappa} = \frac{1}{2\pi} \frac{1}{[2(1 + \delta_{\Omega_1, \Omega_2})]^{1/2}} \times [e^{i\Omega_1\phi_1} e^{i\Omega_2\phi_2} + \kappa e^{i\Omega_2\phi_1} e^{i\Omega_1\phi_2}]. \quad (3.7)$$

The ϕ_1, ϕ_2 coordinates are transformed into ϕ_+ and ϕ_- , previously defined in Eqs. (3.1) and (3.2), taking into account that the Jacobian of that transformation is 2. The resulting Schrödinger equation is

TABLE III. Results of the reduced dimension model for the He-He bending angle. Except for the effective He-Cl₂ distance ($R_{\text{eff}} = \sqrt{1/\langle R^{-2} \rangle}$), which is given in Å, all values are given in cm⁻¹. Reduced dimension energy levels can be directly compared with the full dimensional calculation of Table II.

	$(X, v=0)$	$(B, v=8)$
R_{eff}	3.911	3.993
$\langle B_v j^2 \rangle$	2.123	1.559
ϵ_{00+}	-17.001	-13.522
$E_{v=0}$	-31.728	-25.343
$E_{v=1} - E_{v=0}$	0.540	0.513
$E_{v=2} - E_{v=0}$	1.521	1.435
$E_{v=3} - E_{v=0}$	2.963	2.804

$$\left[\epsilon_v + B_v \langle j^2 \rangle + 2\epsilon_{00+} + \left\langle \frac{-\hbar^2}{4mR^2} \right\rangle \left[\frac{\partial^2}{\partial \phi_+^2} + \frac{\partial^2}{\partial \phi_-^2} \right] + \langle V_{\text{He-He}}(2\phi_-) \rangle \right] F = EF. \quad (3.8)$$

The symmetry-adapted basis functions are written in these coordinates as

$$\Phi'_{\Omega\omega\kappa} = \frac{e^{i\Omega\phi_+}}{(2\pi)^{1/2}} \frac{1}{[\pi(1 + \delta_{\omega,0})]^{1/2}} \cos(\omega\phi_-) \quad \text{for } \kappa = +1, \quad (3.9)$$

$$\Phi'_{\Omega\omega\kappa} = \frac{e^{i\Omega\phi_+}}{(2\pi)^{1/2}} \frac{1}{\pi} \sin(\omega\phi_-) \quad \text{for } \kappa = -1, \quad (3.10)$$

where

$$\Omega = \Omega_1 + \Omega_2, \quad (3.11)$$

$$\omega = \Omega_1 - \Omega_2, \quad (3.12)$$

and where $\omega=0$ is not included in the basis for $\kappa=-1$. Examination of Eq. (3.6) shows that overall rotation and the bending vibration are decoupled within this model. There remains, however, an interesting relationship through the basis set functions, which will be discussed later in connection with the rotationally excited states (Sec. III C). It should be noted that a similar reduced dimension model was proposed in Ref. 17, where the neglected degrees of freedom were frozen (instead of averaged) and the relationship between overall rotation and vibration was not explored.

Results of the calculations performed with the reduced dimension model are presented in Table III. To compare on an equal footing with the full dimensional calculations, the basis functions of Eqs. (3.9) and (3.10) were restricted to $\Omega_1 = \Omega_2 = 0-12$ (the converged energy levels differ only by about 0.02 cm⁻¹). The model reproduces the ground van der Waals state energy to within 0.23 cm⁻¹ for the $(B, v=8)$ state, and to within 0.44 cm⁻¹ for the $(X, v=0)$ state. This is due to the role of excited triatomic configurations (accounted for in the full dimensional calculation and not in the reduced dimension model), which are relatively more important for the X state than for the B state [note that the HeCl₂(X) van der Waals bending frequency is smaller than the HeCl₂(B) one]. For the excited levels ($v=1-3$), reduced and full dimensional energies (referred to as the $v=0$ one) compare very well. Moreover, the reduced dimension model is able to

FIG. 5. Effective He-He potential (in cm^{-1}) as function of ϕ_+ (in degrees) within the reduced dimension model for He₂Cl₂($B, v=8$), together with the resulting energy levels and eigenstate probability densities.

give larger bending excited energies for the X state than for the B state, in agreement with the full dimensional calculations.

In Fig. 5 we present the effective He-He potential $\langle V_{\text{He-He}}(2\phi_+) \rangle$ for ($B, v=8$). In this figure, we also show the probability densities of the four lowest states, together with the eigenenergies of the kinetic plus potential energy operators in Eq. (3.8), that is, $\epsilon_v = E_v - [\epsilon_v + B_v \langle j^2 \rangle + 2\epsilon_{00+}]$. Although the details of the effective potential quantitatively affect the structure of the calculated probability densities, they are qualitatively those of a “particle-in-a-box” Hamiltonian. Probability distributions are quite similar to the full dimensional ones (Fig. 4), although the detailed structure is not reproduced by the reduced dimension calculation, particularly for levels $v=0,1$. The effective He-He potential is useful to understand the origin of the probability distributions. It exhibits very repulsive walls at about $\phi_+ = 20^\circ$ and 160° and shallow and narrow wells at about 23° and 157° , and is very flat otherwise. It is interesting to mention that the nonaveraged He-He potential $V_{\text{He-He}}(R_1=R_2=R_{\text{eff}}, \theta_1=\theta_2=\pi/2, 2\phi_+)$ is similar to $\langle V_{\text{He-He}}(2\phi_+) \rangle$, although the wells are considerably wider and deeper (the well depth is ca. 7.6 cm^{-1}). Thus, the procedure of averaging the He-He potential on the triatomic configurations enlarges the energy of the He-He interaction. For such shallow wells the ground-state level is above the barrier between the two wells ($\epsilon_{v=0} = 0.152 \text{ cm}^{-1}$), and therefore the corresponding wave function is peaked at $\phi_+ = 90^\circ$. A deeper effective potential would yield a lower ground-state energy and the corresponding probability distribution would exhibit two symmetric peaks, one on each side of $\phi_+ = 90^\circ$. In light of the reduced dimension model, we can say that, due to the effect of kinetic energy, the calculated full dimensional ϕ_+ probability distri-

butions for the X and B states [Figs. 3(a) and 4(a)] suggest a “repulsive” He-He interaction within the cluster, causing the preferred cluster geometry to be that for which the He atoms are furthest from each other ($\phi_+ = 90^\circ$, $\phi_1 - \phi_2 = 180^\circ$).

B. $J>0$ states: Full dimensional and rigid rotor model calculations

In Paper I it was reported that the lowest He₂Cl₂ rovibrational energy levels (those that are experimentally probed) can be arranged in two rotational series, corresponding to the ground ($v=0$) and first excited ($v=1$) van der Waals states, and that, within each series, rotationally excited levels could be reproduced by means of a rigid rotor model. Here, we test the validity of the rigid rotor approximation in greater detail.

Energies of the rotationally excited states obtained in the full dimensional calculation are reported in Tables IV–VII, for the ($X, v=0, v=0$), ($X, v=0, v=1$), ($B, v=8, v=0$), and ($B, v=8, v=1$) vibronic states, respectively. The zero of energy for each rotational series is the corresponding van der Waals level previously shown in Table II. From the full dimensional $J=1$ energy levels we have extracted “effective” rotational constants, A_{eff} , B_{eff} , C_{eff} ($A_{\text{eff}} > B_{\text{eff}} > C_{\text{eff}}$), such that the full dimensional energies are exactly $B_{\text{eff}} + C_{\text{eff}}$, $A_{\text{eff}} + C_{\text{eff}}$, $A_{\text{eff}} + B_{\text{eff}}$ (the $J=1$ roots of the asymmetric top Hamiltonian³²). The reason for this choice is that, as will be seen later in the discussion, the averaged rotational constants did not give a good fit to the energy levels. However, the energy levels were found in Paper I to follow a rigid rotor pattern. The most direct way to obtain effective rotational constants and check the validity of the rigid rotor model was then to use the energy difference between $J=1$ and $J=0$ levels. The effective rotational constants obtained in this way are given in Table VIII, for the four states under consideration. Since this rigid rotor model perfectly reproduces the $J=1$ energy levels by construction, one must test this approach by comparing the rigid rotor and full dimensional energy levels for $J>1$. This is done in Tables IV–VII. It can be seen that this model successfully reproduces the full dimensional $J=2,3$ energies, particularly for the upper electronic state. It is surprising that such a simple model works so well for this system where large amplitude motions occur and the frequency of the He-He vibration is of the same order of magnitude as those for rotational motion.

A second approach consists of calculating averaged rotational constants, and comparing them with the ones used in the rigid rotor model. We define a body-fixed frame (xyz) having its origin in the center of mass of Cl₂ (which coincides with the expectation value of the center of mass of the total system), and oriented so that the z axis is parallel to the Cl₂ axis and the x axis bisects the angle between the projections of the R_1 and R_2 vectors in the plane perpendicular to the Cl₂ axis containing its center of mass. This is a principal axis frame; the expectation values of the products of inertia (I_{xy}, I_{xz}, I_{yz}) are zero. With this choice, a rigid rotor Hamiltonian can be written as

$$H_{rr} = XJ_x^2 + YJ_y^2 + ZJ_z^2, \quad (3.13)$$

TABLE IV. Rotational series of $\text{He}_2\text{Cl}_2(X, v=0, \nu=0)$. Energies are in cm^{-1} . The zero for energies is the $J=0$ energy. Full dimensional results are compared with rigid rotor (RR) energy levels from an asymmetric top Hamiltonian (a) using effective rotational constants (such that the full dimensional $J=1$ energies are reproduced), and (b) using rotational constants averaged over the $J=0$ full dimensional wave functions. See the text for more details.

Full dimensional			RR model			
			(Effective rot. cons.)	(Averaged rot. cons.)		
J	$\varepsilon\eta\kappa$	E	Sym	E	E	$C_2^x C_2^y C_2^z$
0	+++	0	A	0	0	+++
1	− + −	0.27	B_a	0.27	0.25	− + −
	− − +	0.33	B_b	0.33	0.27	− − +
	+ − −	0.37	B_c	0.37	0.32	+ − −
2	+++	0.79	A	0.80	0.72	+++
	+ − −	0.82	B_c	0.83	0.73	+ − −
	− − +	0.95	B_b	0.96	0.86	− − +
	− + −	1.10	B_a	1.13	0.93	− + −
	+++	1.11	A	1.14	0.96	+++
3	− + −	1.52	B_a	1.56	1.39	− + −
	− − +	1.53	B_b	1.57	1.39	− − +
	+ − −	1.79	B_c	1.83	1.64	+ − −
	+++	1.91	A	1.95	1.68	+++
	− + −	1.96	B_a	2.02	1.78	− + −
	− − +	2.16	B_b	2.34	1.92	− − +
	+ − −	2.16	B_c	2.35	1.93	+ − −
	+++					+++

where the rotational constants are the expectation values

$$P = \langle \Psi_{(J=0)} | \frac{\hbar^2}{2I_{pp}} | \Psi_{(J=0)} \rangle, \quad (3.14)$$

where $P=X, Y, Z$ and $I_{pp}(pp=xx, yy, zz)$ are the principal moments of inertia. Once the Cartesian coordinates giving the position of each nucleus in the body-fixed frame are related to R_i , θ_i , ($i=1,2$), ϕ_- , and r , the moments of inertia are readily given as functions of the internal coordinates. The

six-dimensional integral involved in Eq. (3.14) was performed using Gauss–Legendre points for the angular coordinates and equally spaced grids for the radial coordinates.

Averaged and effective rotational constants are compared in Table VIII. It can be seen that the average values follow qualitatively the same trend as the effective ones, but are about 10% smaller, except for the $(X, \nu=1)A$ constant, where $\langle A \rangle$ is slightly larger than A_{eff} . As a consequence, the resulting rigid rotor energy levels, also reported in Tables

TABLE V. Same as Table IV for $\text{He}_2\text{Cl}_2(X, v=0, \nu=1)$.

Full dimensional			RR model			
			(Effective rot. cons.)	(Averaged rot. cons.)		
J	$\varepsilon\eta\kappa$	E	Sym	E	E	$C_2^x C_2^y C_2^z$
0	− − −	0	A	0	0	− − −
1	+++	0.28	B_a	0.28	0.26	− − +
	+ − +	0.28	B_b	0.28	0.27	− + −
	− + +	0.29	B_c	0.29	0.29	+ − −
2	− − −	0.84	A	0.84	0.76	+++
	− + +	0.84	B_c	0.84	0.77	+ − −
	+ − +	0.87	B_b	0.86	0.82	− + −
	+ + −	0.89	B_a	0.86	0.85	− − +
	− − −	0.90	A	0.87	0.86	+++
3	+++	1.67	B_a	1.68	1.51	− − +
	+ − +	1.67	B_b	1.68	1.51	− + −
	− + +	1.74	B_c	1.71	1.61	+ − −
	− − −	1.74	A	1.71	1.63	+++
	+++	1.77	B_a	1.73	1.67	− − +
	+ − +	1.82	B_b	1.73	1.74	− + −
	− + +	1.82	B_c	1.73	1.74	+ − −
	− − −					− − −

TABLE VI. Same as Table IV for He₂Cl₂(*B*,*v*=8,*ν*=0).

Full dimensional			RR model			
			(Effective rot. cons.)		(Averaged rot. cons.)	
<i>J</i>	$\epsilon\eta\kappa$	<i>E</i>	Sym	<i>E</i>	<i>E</i>	$C_2^xC_2^yC_2^z$
0	+++	0.	<i>A</i>	0	0	+++
1	− − +	0.21	<i>B_a</i>	0.21	0.18	− − +
	− + −	0.23	<i>B_b</i>	0.23	0.21	− + −
	+ − −	0.27	<i>B_c</i>	0.27	0.25	+ − −
2	+++	0.59	<i>A</i>	0.59	0.53	+++
	+ − −	0.59	<i>B_c</i>	0.60	0.54	+ − −
	− + −	0.72	<i>B_b</i>	0.73	0.65	− + −
	− − +	0.79	<i>B_a</i>	0.78	0.73	− − +
	+++	0.81	<i>A</i>	0.81	0.75	+++
3	− − +	1.13	<i>B_a</i>	1.13	1.03	− − +
	− + −	1.13	<i>B_b</i>	1.13	1.03	− + −
	+ − −	1.37	<i>B_c</i>	1.38	1.24	+ − −
	+++	1.40	<i>A</i>	1.40	1.28	+++
	− − +	1.48	<i>B_a</i>	1.51	1.36	− − +
	− + −	1.62	<i>B_b</i>	1.62	1.52	− + −
	+ − −	1.62	<i>B_c</i>	1.63	1.52	+ − −

IV–VII, are consistently lower than the full dimensional ones. Nevertheless, the energy level structure is correctly predicted. Moreover, full dimensional and rigid rotor states are well correlated regarding symmetry properties. If one considers that the rigid structure of the cluster consists of both He atoms lying on a ring perpendicular to the Cl₂ cluster (a reasonable assumption in view of the *J*=0 probability distributions), and with the help of Fig. 6, it is seen that the relationship between the twofold rotations C_2^x , C_2^y , and C_2^z (rigid rotor symmetry operations) and the permutation-inversion operations P_ϵ , P_η , and P_κ (full dimensional operations) is

$C_2^x=P_\eta P_\kappa,$

(3.15)

$C_2^y=P_\epsilon P_\kappa,$

(3.16)

$C_2^z=P_\epsilon P_\eta.$

(3.17)

It is found that, for every state of Tables IV–VII, eigenvalues of the full dimensional and rigid rotor symmetry operators are exactly related as given above. Therefore, this second rigid structural model, although not giving a quantitative agreement regarding energy levels, provides the correct symmetry properties of the full dimensional states.

TABLE VII. Same as Table IV for He₂Cl₂(*B*,*v*=8,*ν*=1).

Full dimensional			RR model			
			(Effective rot. cons.)		(Averaged rot. cons.)	
<i>J</i>	$\epsilon\eta\kappa$	<i>E</i>	Sym	<i>E</i>	<i>E</i>	$C_2^xC_2^yC_2^z$
0	− − −	0.	<i>A</i>	0	0	+++
1	+++	0.19	<i>B_a</i>	0.19	0.18	− − +
	+ − +	0.24	<i>B_b</i>	0.24	0.22	− + −
	− + +	0.25	<i>B_c</i>	0.25	0.23	+ − −
2	− − −	0.58	<i>A</i>	0.58	0.53	+++
	− + +	0.62	<i>B_c</i>	0.62	0.57	+ − −
	+ − +	0.65	<i>B_b</i>	0.65	0.60	− + −
	+ + −	0.79	<i>B_a</i>	0.80	0.74	− − +
	− − −	0.79	<i>A</i>	0.80	0.74	+++
3	+++	1.16	<i>B_a</i>	1.16	1.06	− − +
	+ − +	1.19	<i>B_b</i>	1.19	1.09	− + −
	− + +	1.24	<i>B_c</i>	1.24	1.15	+ − −
	− − −	1.36	<i>A</i>	1.38	1.27	+++
	+++	1.36	<i>B_a</i>	1.38	1.28	− − +
	+ − +	1.61	<i>B_b</i>	1.65	1.52	− + −
	− + +	1.61	<i>B_c</i>	1.65	1.52	+ − −

TABLE VIII. Effective rotational constants ($A_{\text{eff}}, B_{\text{eff}}, C_{\text{eff}}$) and averaged ones ($A_{\text{av}}, B_{\text{av}}, C_{\text{av}}$) (obtained by averaging over the $J=0$ vibrational wave functions), for different He_2Cl_2 vibronic states. The principal axes associated with the averaged rotational constants are indicated in parentheses (the molecular fixed frame used is that depicted in Fig. 6).

	$(X, \nu=0)$		$(B, \nu=8)$	
	$\nu=0$	$\nu=1$	$\nu=0$	$\nu=1$
A_{eff}	0.214	0.145	0.144	0.151
A_{av}	0.171(y)	0.149(z)	0.133(z)	0.133(z)
B_{eff}	0.159	0.145	0.126	0.102
B_{av}	0.146(z)	0.138(y)	0.109(y)	0.093(y)
C_{eff}	0.115	0.139	0.082	0.093
C_{av}	0.103(x)	0.121(x)	0.075(x)	0.085(x)

To investigate the discrepancies between the averaged and the effective rotational constants, we first checked that the internal coordinate probability distributions for the $J=1$ states are almost identical to those found for the $J=0$ states. Thus, the discrepancy cannot be attributed to a variation of the “averaged geometry” with total angular momentum. We have also carried out many convergence tests to conclude that such a 10% difference cannot be due to a numerical error. The reason that this second rigid rotor model does not work as well as the “empirical” one is probably due to the body-fixed axis frame, which does not optimize the separation between vibration and rotation. For this floppy system, a better procedure would be to define new inertial axes satisfying the Eckart conditions,³³ and to calculate average rotational constants with respect to the new body-fixed frame. Such Eckart-averaged rotational constants should compare better with the effective ones. Derivation of Eckart

FIG. 6. Effect of the permutation-inversion operators and rigid rotor twofold rotations on He_2Cl_2 , assuming that both rare gas atoms lie on a plane (the xy plane) perpendicular to the Cl_2 axis (the z axis) and that the $\text{He}-\text{Cl}_2$ distances are equal for both He atoms. It can be seen that rigid rotor operations are related to the permutation-inversion operations as follows: $C_2^x = P_\eta P_K$, $C_2^y = P_\epsilon P_K$, $C_2^z = P_\epsilon P_\eta$.

FIG. 7. Rotational constants (X, Y, Z) for the assumed rigid geometry of He_2Cl_2 displayed in Fig. 6, and with respect to the molecular axes also depicted in that figure. The Cl_2 internuclear distance is $r = 2.644 \text{ \AA}$ (the effective distance such as $\hbar/2\mu r^2$ equals the $(B, \nu=8)$ Cl_2 rotational constants). The $\text{He}-\text{Cl}_2$ distance (equal for both He atoms) is $3.85 \text{ \AA}$. Such geometrical rotational constants are presented as functions of ϕ_- , where $2\phi_-$ is the $\text{He}-\text{He}$ angle. Also shown are the effective rotational constants for $(B, \nu=8, \nu=0)$ and $(B, \nu=8, \nu=1)$ states. It can be seen that the geometrical constants are close to the effective ones for $\phi_- \approx 65^\circ$ and 47° , for $\nu=0$ and $\nu=1$, respectively.

molecule fixed axes in terms of internal coordinates different from the traditional normal coordinates has been discussed, for example, by Ernesti and Hutson for the $\text{Ar}-\text{CO}_2$ van der Waals molecule³⁴ and more recently in a series of papers by Wei and Carrington.³⁵ We have not attempted, however, to perform this task here. Nevertheless, the fact that the present averaged rotational constants give at least a zero-order approximation of the effective ones and that the symmetry properties of the full dimensional states are well predicted leads one to assume that the optimized Eckart frame ($x'y'z'$) must not be too different from the (xyz) frame used here (that is, the angle between x and x' axes should be small, etc.).

Our next goal is to relate the effective rotational constants to geometrical structures of the complex, by comparing them with rotational constants obtained from hypothetical geometries of the system (“geometrical” rotational constants). The geometrical rotational constants are computed with respect to the nonoptimized (xyz) frame, expecting that this approximation does not change the qualitative conclusions. Again, it is assumed that both He atoms lie on a ring perpendicular to the Cl_2 axis. The effective $\text{Cl}-\text{Cl}$ distance r_{eff} is such that $B_\nu = \hbar^2/(2\mu r_{\text{eff}}^2)$. The remaining parameters (the $\text{He}-\text{Cl}_2$ distance, R , and the $\text{He}-\text{He}$ angle, $2\phi_-$) are varied to reproduce the values of the effective rotational constants. The result for $(B, \nu=8)$ is shown in Fig. 7, where the X, Y, Z geometrical constants for $R = 3.85 \text{ \AA}$ are displayed as functions of ϕ_- . It can be seen that for $\phi_- \approx 65^\circ$ and 47° , the resulting rotational constants agree with the effective ones for $\nu=0$ and $\nu=1$, respectively. These geometries correspond to those suggested by us as the aver-

aged cluster geometries in Ref. 20. Indeed, for $\nu=1$, the averaged geometry (as expected from the $J=0$ probability distributions) matches the optimal pointwise geometry [see in Fig. 4(b) the ϕ_- distribution peaked at $\approx 50^\circ$]. This is, however, not the case for $\nu=0$, because $\phi_- \approx 90^\circ$ [the average value of Fig. 4(a)] would lead to rotational constants quite different from the effective ones (see Fig. 6). From our calculation of averaged rotational constants, we believe that this difference is due to the broad probability distribution in ϕ_- and the complex dependence of the moments of inertia with this degree of freedom, so that $(\hbar^2/2) \times \langle \Psi(\phi_-) | I_{pp}^{-1} | \Psi(\phi_-) \rangle$ is quite different from $(\hbar^2/2) I_{pp}^{-1}$ ($\phi=90^\circ$). It is well known that rotational parameters obtained from spectroscopic data for semirigid molecules do not give direct information on the equilibrium positions of the potential energy surface, but rather on the averaged molecular geometry.³⁶ The present result shows that for a very floppy system, geometrical inferences from moments of inertia can be quite misleading without reference to a model specifically developed for the molecule under study.

C. Combining the rigid rotor model and the one-dimensional model for the He–He bending: Assigning permutation-inversion labels to rigid rotor states

As reported in the preceding paragraphs, the rovibrational structure of the lowest energy levels of He₂Cl₂($X, \nu=0$) and ($B, \nu=8$) can be satisfactorily reproduced by means of a reduced dimension model for the He–He bending together with a rigid structural model for the rotationally excited states. The combined use of these models is a useful and inexpensive tool to predict the excitation spectra for floppy tetra-atomic clusters, and extract structural and dynamical information from fits to measured spectra. However, a remaining question is whether this simplified approach can predict the behavior of the states under permutation-inversion operations. Such an information is essential to assign proper statistical weights to the transitions involved in an excitation spectrum. In view of Eqs. (3.15), (3.16), and (3.17), it might appear that the eigenvalues of the permutation-inversion operators can be extracted from the behavior of the rigid rotor states under the twofold rotations, given by the eigenvalues of C_2^x , C_2^y and C_2^z . However, since $C_2^x = C_2^y C_2^z$, $C_2^y = C_2^z C_2^x$, and $C_2^z = C_2^x C_2^y$, Eqs. (3.15), (3.16), and (3.17) are not linearly independent: the rigid rotor model alone is unable to predict the behavior of asymmetric top states under the permutation-inversion operators, and an unambiguous assignment of eigenvalues is not possible. It is necessary to include further information on the vibrational degrees of freedom and their relationship to the rotational degrees of freedom.

The reduced dimension model of Sec. III A is in fact a two-degree-of-freedom model for the He–He bending and overall rotation about the Cl₂ axis. Although these modes are decoupled in the model Hamiltonian, the symmetry-adapted basis functions [Eqs. (3.9) and (3.10)] are closely related by means of their quantum number Ω and ω . They are determined by the sum and the difference, respectively, of Ω_1 and Ω_2 [Eqs. (3.11) and (3.12)]. Since the latter are integer num-

TABLE IX. Allowed transitions between asymmetric top (RR) states for He₂Cl₂($B, \nu, v \leftarrow (X, v'', v''')$). B_x and B_y levels are forbidden for $\nu=\text{even}$, and B_z, A levels for $\nu=\text{odd}$, due to the spin statistics of He nuclei. The correspondence with the permutation-inversion labels is also given, as well as the statistical weight (3 or 5 for symmetric and antisymmetric states under Cl exchange, respectively).

$B \leftarrow X$ $\nu \leftarrow \nu''$	RR transition	$(\epsilon, \eta, \kappa) \leftarrow (\epsilon'', \eta'', \kappa'')$	Statistical weight
even $\leftarrow$ even	$B_z \leftarrow A$	$(- - +) \leftarrow (+ + +)$	3
	$A \leftarrow B_z$	$(+ + +) \leftarrow (- - +)$	5
odd $\leftarrow$ odd	$B_y \leftarrow B_x$	$(+ - +) \leftarrow (- + +)$	3
	$B_x \leftarrow B_y$	$(- + +) \leftarrow (+ - +)$	5

bers, Ω and ω are integers with the *same parity*. Let us suppose, for instance, that $\kappa = +1$ (the He–He exchange eigenvalue) and Ω is even. Then, the vibrational wave function will be expressed as a linear combination of $\cos(\omega\phi_-)$ with ω even, and it will exhibit a maximum or a minimum at $\phi_- = \pi/2$. Thus, it will represent a vibrational state with ν even. Working out the other combinations of κ and Ω , the following relationship is obtained:

$$\kappa = (-1)^\nu (-1)^\Omega. \quad (3.18)$$

The quantum number Ω is the projection of the total angular momentum onto the Cl–Cl axis (the z axis). Although in the full dimensional treatment this is not an exact quantum number, it was checked that the *parity* of Ω is a good quantum number and that Eq. (3.18) holds for all the calculated full dimensional states. Ω correlates with K , the projection of J onto the body-fixed z axis in the rigid rotor model (we assume that a similar correlation holds for an optimized Eckart frame). The asymmetric top wave functions which are even (odd) under the C_2^z rotation are built as linear combinations of even (odd) free-rotor functions having even (odd) K . Therefore, we can write

$$\kappa = (-1)^\nu C_2^z, \quad (3.19)$$

which gives the symmetry under He–He exchange of an asymmetric top state, depending on the parity of the accompanying He–He vibrational state. It can be seen that all parity labels of Tables IV–VII obey Eq. (3.19). This is the needed “recipe” for spectrum simulations for this type of cluster: the parity of the He–He vibrational state has to be examined in addition to the parity of the rigid rotor states, since the helium atoms can (and do) exchange by vibration (it can be seen from Fig. 6 that combining $2\phi_- \rightarrow 2\pi - 2\phi_-$ with a C_2^z rotation is equivalent to He exchange, and we have seen in Figs. 3 to 5 that the He–He bending levels have a definite parity with respect to the $\phi_- \rightarrow \pi - \phi_-$ operation since the bending wave function has a non-negligible amplitude in the region of the barrier).

Table IX summarizes the set of allowed rigid rotor transitions (those involving states symmetric under He exchange) within the present model, together with the associated permutation-inversion labels and transition statistical weights.

FIG. 8. Experimental spectrum (dashed lines) for the parity selected transition $[(B, v=8, \eta=+) \leftarrow (X, v''=0, \eta''=-)]$ compared with model simulation (solid lines). Intensity is in arbitrary units and photon frequency is given in cm^{-1} . Experimental data are from Ref. 12. See the text for details on the model simulation. Individual transitions are drawn as sticks (solid and dashed lines correspond to $v=0 \leftarrow v''=0$ and $v=1 \leftarrow v''=1$ transitions, respectively).

D. Model simulations of experimental spectra: $\text{He}_2\text{Cl}_2[(B, v=8-13) \leftarrow (X, v''=0)]$

In this section, we apply the He-He vibration-rigid rotor model to the simulation of excitation spectra of He_2Cl_2 for different final dihalogen vibrational states. The procedure involves considering the transitions $(B, v, v=0) \leftarrow (X, v'', v''=0)$ and $(B, v, v=1) \leftarrow (X, v'', v''=1)$ using asymmetric top wave functions, and taking into account the selection rules of Table IX. Each electronic and vibrational state is characterized by a set of fitted rotational constants, obtained from assumed molecular geometries as follows. Bond lengths and angles determining molecular geometries are used as fitting parameters. We assume that the He atoms lie in a plane perpendicular to the Cl_2 axis and that the He- Cl_2 distance is the same for both He atoms. The geometrical parameters are: the Cl_2 internuclear distance, $r_{X,B}$, the He- Cl_2 bond length, $R_{X,B}(v)$, and the He- Cl_2 -He bond angle, $2\phi_{X,B}(v)$. The Cl_2 internuclear distance is obtained from the Cl_2 rotational constant in the corresponding vibronic state: $r = \hbar / (2\mu B_v)^{1/2}$. Another parameter gives the band origin for transitions between $v=1$ states, determined by the difference of bending frequencies in the B and X states ($w_B - w_X$). Additional parameters are the spectral shift (the band origin with respect to the Cl_2 band), the cluster temperature, and the homogeneous and laser linewidths. Because the two contributions to the linewidth are highly correlated, we have first determined the laser linewidth from simulations of the corresponding $\text{Cl}_2(B, v_B) \leftarrow (X, v_X)$ band, which is then used as a fixed parameter in the analysis of the He_2Cl_2 band.

In Fig. 8 we present a comparison between spectrum simulations and experiment for the parity-selected transition $(B, v=8, \eta=+) \leftarrow (X, v''=0, \eta''=-)$. Details on the experimental technique and measurement conditions are reported

in Ref. 12. The bond lengths used in the calculation are $R_X(0)=3.65 \text{ \AA}$, $R_X(1)=3.75 \text{ \AA}$, $R_B(0)=R_B(1)=3.85 \text{ \AA}$, and the angles are $\phi_X(0)=\phi_B(0)=64^\circ$, $\phi_X(1)=\phi_B(1)=45^\circ$ (note that the bond angles are $2\phi_X, 2\phi_B$). These values were obtained from slight variations around those that optimally reproduce the effective rotational constants of Table VIII. In the same way, the $v=1$ band origin was readjusted from the theoretical one of $w_B - w_X = -0.05 \text{ cm}^{-1}$ to -0.11 cm^{-1} in order to improve the agreement with the measured spectrum. Although we have not attempted to perform an exhaustive analysis, we have found that the band shape is quite sensitive to moderate variations of the geometrical parameters but less sensitive to slight variations. Regrettably, the homogeneous linewidth could not be obtained as it is much smaller than the laser linewidth for this Cl_2 vibrational state. Owing to the simplicity of the model, it can be said that a satisfactory agreement with experiment is attained, as the positions and intensities of most of the resolved peaks are successfully reproduced.

The next step is to apply the present method to extract information for $\text{He}_2\text{Cl}_2(B)$ in different Cl_2 vibrational states, $v=10-13$, for which no full dimensional calculations have been carried out. For these vibrational levels, the homogeneous linewidth is large enough so that reliable values can be obtained. On the other hand, the spectra become less (rotationally) resolved due to the increasing magnitude of the natural linewidth. In addition, the $v=10-13$ spectra were not parity selected, and were recorded with a lower laser resolution than the parity-selected spectrum of $v=8$. Thus, it is not possible to extract structural information for the higher v levels. For this reason, we keep the same values of the geometrical parameters used for $v=8$, except for r_B , which is varied according to the corresponding Cl_2 rotational constant. In Fig. 9 we present a comparison between measurements and model simulations for $v=10-13$. It is seen that the band shapes are in good agreement. The right-hand (blue) tails, which are the regions most sensitive to the homogeneous linewidth, are very well reproduced. Values for the linewidths are given in Table X. Since the laser linewidth is about 0.2 cm^{-1} , a reasonable estimate for the accuracy of the homogeneous linewidth determination is 0.05 cm^{-1} . Therefore, the value extracted for $v=10$ is only approximate. The spectral shifts obtained are, to within $\pm 0.1 \text{ cm}^{-1}$, twice those of HeCl_2 .^{37,38} This result is in accordance with the theoretical prediction that He_2Cl_2 dissociation energy is roughly twice the HeCl_2 one.

Insight into cluster fragmentation processes can be obtained from the homogeneous linewidth. If bond breaking occurs mainly sequentially [Eq. (1.1)] and the departure of one He atom is unaffected by couplings with the other He atom, it is expected that the homogeneous width will be about twice that of HeCl_2 (as the initial parent molecule) for the same v , $\Gamma(\text{He}_2\text{Cl}_2(B, v)) \approx 2\Gamma(\text{HeCl}_2(B, v))$.³⁹ The He_2Cl_2 widths obtained by fits to the observed spectra are presented in Table X, together with $2\Gamma(\text{HeCl}_2(B, v))$ (taken from Ref. 37). It is found that the widths $\Gamma(\text{He}_2\text{Cl}_2(B, v))$ are always slightly larger than $2\Gamma(\text{HeCl}_2)$, although the differences are within experimental error. The small increase in the dissociation rate over the simple sequential estimate

FIG. 9. Non-parity-selected spectra $[(B,v) \leftarrow (X,v''=0)]$ for $v=10-13$. Experimental data and model simulations are shown in dashed and solid lines, respectively. Intensity is in arbitrary units and photon frequency is given in cm^{-1} . The blue tails of the spectra are very well reproduced by the model, so reliable homogeneous linewidths can be estimated. See the text for more details.

could be due to the role of direct $\Delta v = -1$ dissociation of both He atoms in addition to the sequential process. This interpretation is supported by the experimental observation of $v-1$ population, also found (4%) in reduced-dimensional

TABLE X. He₂Cl₂ homogeneous linewidths as obtained from model simulations of excitation spectra $(B,v) \leftarrow (X,v'')$, $v=10-13$. For the sake of comparison, the HeCl₂ widths multiplied by two are shown for the same vibrational states. Theoretical results from reduced dimension quantum-mechanical (RDQ) calculations (Ref. 40) and quasiclassical trajectories (QCT) (Ref. 21) are also given.

	$v=10$	$v=11$	$v=12$	$v=13$
He ₂ Cl ₂ (this work)	0.10	0.13	0.21	0.48
$2 \times \text{HeCl}_2$ (Ref. 37)	0.06	0.11	0.20	0.43
RDQ (Ref. 40)	0.24	0.33	0.45	0.60
QCT (Ref. 21)				0.31

dynamical calculations by Le Quéré and Gray⁴⁰ on the same system. Another possibility is that, within the sequential process, the departure of the first He atom is accelerated by (direct or mediated by Cl₂) couplings with the second He atom. This was the interpretation given by Schatz *et al.*⁴¹ from quasiclassical trajectory simulations of Ne₂I₂ fragmentation. Experiments in the time domain providing rates for the different final Cl₂ vibrational channels and for the He-Cl₂ intermediate would be very useful in the understanding of the detailed fragmentation mechanism of the cluster.⁴²

Some published theoretical results are also shown in Table X: the rates obtained by Le Quéré and Gray in reduced dimension quantum-mechanical calculations⁴⁰ and the $v=13$ rate from full dimensional quasiclassical trajectory (QCT) calculations.²¹ The theoretical simulations were performed using potential energy surfaces whose triatomic HeCl₂ part does not reproduce perfectly well the observed HeCl₂ rates. Therefore, the differences between calculated and experimentally measured He₂Cl₂ widths can be first explained by the use of a insufficiently accurate potential energy surface. In addition, we think that the large values of the Le Quéré and Gray's rates are also due to the neglect of the zero-point energy of the He-Cl₂ bending motion, which is frozen in the model. Campos Martínez *et al.*,⁴³ in their theoretical study of Ne₂I₂, have shown that including a simple energy correction in the reduced dimension model makes the widths substantially smaller.

IV. CONCLUSION

Full dimensional quantum-mechanical calculations on the rovibrational structure of the He₂Cl₂ cluster have been performed. The lowest energy levels correspond to the ground and excited states in the bending mode associated to the angle formed between the two He-(center of mass of Cl₂) bonds. Except for the distribution in the azimuthal angles, the wave function probability distributions are identical to those of the triatomic complex HeCl₂ in the same electronic and vibrational state. Although there is an extensive delocalization of the He atoms around a ring perpendicular to Cl₂, the averaged cluster geometry for the ground state is planar with He atoms at opposite ends of a straight line perpendicular to the Cl₂ axis. A reduced dimension model for the He-He bending provides very good approximate energy levels and gives insight into the cluster structure. The effective potential for He₂ within the cluster yields

two symmetrical wells corresponding to two equilibrium positions of the He atoms, δ_e and $2\pi - \delta_e$, the latter being related to the former by exchanging the helium atoms. Due to the very small interaction between the He atoms and due to their light masses, the ground-state level is above the barrier separating the two wells. Thus, the maximum of the ground-state wave function corresponds to a He–He angle of 180° , in accordance with the full dimensional averaged geometry. This situation does not occur for other systems that might be thought to behave similarly to He_2Cl_2 . For instance, in clusters with Ne atoms, the Ne–Ne interaction is stronger, which makes the barrier at the collinear $\text{Ne}-(\text{Cl}_2)\text{-Ne}$ configuration higher. Also, the zero-point energy is much smaller than the Ne–Ne well depth. Thus, the ground (symmetric) and first excited (antisymmetric) states are nearly degenerate and their wave functions are localized near the equilibrium positions. Thus, either the symmetric or the antisymmetric bending state can be combined with a given rigid rotor state in order to build a symmetric state under Ne–Ne exchange, and the fitting of the excitation spectra by means of a rigid rotor model can be carried out in the standard way. Thus, the effect of spin statistics is much more dramatic for He_2Cl_2 than it is for Ne_2Cl_2 .

The rotationally excited energy levels for low J are successfully reproduced by means of a simple rigid rotor model where the rotational constants are chosen to reproduce the $J=1$ energy levels. The success of this rigid structural model is surprising in view of the very large amplitude motions of the cluster. This remarkable property of the rigid rotor Hamiltonian was noted by Nesbitt and Naaman,⁴⁴ and is due to the fact that only low rotational levels are populated in the experiment. The cluster geometry which effectively reproduces the rotationally excited levels differs from the averaged cluster geometry in that the He–He bending angle is smaller ($\approx 130^\circ$). Structural information obtained from analysis of rotationally excited levels does not match the averaged cluster geometry. Using vibrationally averaged rotational constants, the same rigid rotor model provides only semiquantitative agreement with the full dimensional energy levels. We believe that this is due to the use of a molecular frame where the separation between rotation and vibration is not optimized. However, even in this nonoptimized body-fixed frame, the correlation between the rigid rotor rotations and the permutation-inversion operations can be established. A consequence of this analysis is that the rigid rotor model alone cannot predict the symmetry of the wave functions under permutation-inversion operations. However, the reduced dimension model for the He–He bending provides the relationship between the He permutation symmetry and the rotational and vibrational quantum numbers. With the aid of this model we have been able to provide correct permutation-inversion labels for the rigid rotor states and, hence, statistical weights for asymmetric top transitions. Taking into account these considerations, it is shown that the observed He_2Cl_2 excitation spectra can be well simulated by means of rigid structural models.

This model allows us to extract homogeneous linewidths from the spectra of the ($B, v=10-13$) levels of He_2Cl_2 . The analysis suggests that the fragmentation mechanism is

mainly sequential, but that the departure of the first He atom is accelerated either by collisions with the remaining rare gas atom or due to a competing fragmentation channel, such as a direct three-body fragmentation process.

Theoretical studies on rare gas–halogen clusters consisting of accurate quantum-mechanical calculations together with developments of simple models prove to be a very fruitful way for the understanding of these systems. Such models may be extended to the study of clusters containing more rare gas atoms. Quantum Monte Carlo calculations by McMahon and Whaley¹⁸ and, more recently, by Lewerenz¹⁹ (using different interaction potentials), show that in the ground-state structure of He_nCl_2 the He atoms are delocalized roughly in the equatorial ring about the diatomic, for $n < 7$. Therefore, a generalization of the model presented here for n He atoms ($n < 7$) should provide interesting insight into the structure of the ground- and low-lying excited states of those systems. In addition, the rotational structure as a function of n could be analyzed and relationships with recent studies of the He_nSF_6 ⁷⁻⁹ and He_nOCS ¹⁰ small clusters could be established. Work in this direction is in progress.

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