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Calculation of the rovibrational $B \leftarrow X$ excitation spectrum of the He_2Cl_2 cluster

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Three-dimensional quantum mechanical calculations on the rovibrational $B \leftarrow X$ excitation spectrum of He_2Cl_2 are presented, and give excellent agreement with recent experiments. It is also shown that the spectrum can be fit by a rigid rotor if He exchange symmetry and overlapping He–He bending excitations are taken into account.

INTRODUCTION

Recently, Sands, Bieler, and Janda¹ have studied that $B \leftarrow X$ high resolution excitation spectrum and the vibrational predissociation of the He_2Cl_2 van der Waals (vdW) complex. In other related vdW molecules, such as HeCl_2 ,² Ne_2Cl_2 ,³ and Ar_2Cl_2 ,⁴ Janda and co-workers had found that a rigid rotor asymmetric top model worked remarkably well, showing that the concept of an “average geometry” was still appropriate despite the large amplitude motions in the internal degrees of freedom of those molecules. But they were unable to fit the He_2Cl_2 spectrum by means of a rigid rotor analysis, which led them to propose this complex as one of the floppy molecules. In a previous theoretical work, García-Vela *et al.*⁵ had noticed the extremely diffuse motions of the He atoms in a similar molecule, He_2I_2 . More recently, Bačić *et al.*,⁶ in a quantum Monte Carlo calculation of the ground state of He_2Cl_2 , reinforced the picture of an exceptionally fluxional complex.

In this communication, we present accurate quantum mechanical calculations for the rovibronic $B \leftarrow X$ transition in He_2Cl_2 . The goal is to gain understanding in the nature of the interaction between the vibrational and rotational degrees of freedom in that complex. In He_2Cl_2 , because of the very weak He–He attraction, the He–Cl₂–He “bending” motion is expected to be of very low frequency and hence to couple with the overall rotation of the complex about an axis parallel to the Cl–Cl bond. The potential energy surface is constructed as a sum of the pairwise Cl–Cl and He–Cl₂ interactions which gave accurate results for HeCl_2 , and of the He–He interaction. All the permutation and inversion symmetries are considered. In particular, the role played by the spin statistics of the ⁴He nuclei (spin zero) is investigated. The consequences on fitting the He_2Cl_2 spectrum to a rigid rotor model in order to get structural parameters are explored. A more detailed analysis of the results, together with their extension to ³He clusters, will be presented in a forthcoming paper.

POTENTIAL ENERGY SURFACE AND METHODOLOGY

The potential energy surface was constructed as a sum of the following pairwise interactions: the $V_{\text{Cl-Cl}}$ X and B potentials (as well as the rotational constants B_v) from Coxon,⁷ the $V_{\text{Cl}_2\text{-He}}$ interactions in the $Y \equiv X$ or B electronic state from Beneventi *et al.*,⁸ which describe very well spectro-

scopic and dynamical data of the triatomic; and the semi-empirical $V_{\text{He-He}}$ interaction by Aziz and Slaman,⁹ which characterizes quite well a large range of experimental data and is consistent with *ab initio* calculations of the He_2 ground electronic state.

In the center-of-mass frame, we used the following coordinates: $\mathbf{r}(r, \theta_r, \phi_r)$, the vector joining the two chlorine nuclei, referred to space-fixed axes, and the valence-type coordinates $\mathbf{R}_i(R_i, \theta_i, \phi_i)$ where $\mathbf{R}_i$ points at the i th He atom from the center of mass of Cl_2 , referred to the body-fixed frame which has its z axis parallel to $\mathbf{r}$. With these coordinates, the Hamiltonian can be written as^{5,10,11}

$$H(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2) = H_{\text{Cl}_2}(r) + \frac{j^2}{2\mu r^2} + \sum_{i=1,2} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R_i^2} + \frac{l_i^2}{2mR_i^2} + V_{\text{Cl}_2\text{-He}}(r, R_i, \theta_i) \right) + V_{\text{He-He}}(\mathbf{R}_1, \mathbf{R}_2) - \frac{\hbar^2}{2M_{\text{Cl}}} K_{\mathbf{R}_1\mathbf{R}_2}. \quad (1)$$

In Eq. (1), H_{Cl_2} is the vibrational Hamiltonian of Cl_2 and $\mathbf{j}$ its angular momentum. The third term is the sum of the vdW triatomic Hamiltonians for each He atom, l_i being the angular momentum associated with $\mathbf{R}_i$ and $m = M_{\text{He}}M_{\text{Cl}_2}/(M_{\text{He}} + M_{\text{Cl}_2})$. The last term in Eq. (1) is a crossed kinetic term, with $K_{\mathbf{R}_1\mathbf{R}_2}$ involving only crossed differentiation with respect to $\mathbf{R}_1$ and $\mathbf{R}_2$, and is due to the use of valence coordinates for the He atoms. Because of the relative masses of He and Cl_2 , it will only be important for high angular excitations¹¹ and hence it can be neglected since we are dealing with the lowest energy levels.

Due to the large frequency difference between the Cl_2 and the van der Waals vibrations, r is decoupled from the other degrees of freedom² and the total wave function can be written as $\Theta_v^Y(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2) = \chi_v^Y(r) \Psi_v^Y(\hat{r}, \mathbf{R}_1, \mathbf{R}_2)$, where Ψ_v^Y is an eigenfunction of $H^{Yv} = \langle \chi_v^Y | H | \chi_v^Y \rangle$ and χ_v^Y is a vibrational function of Cl_2 in the $Y(Y \equiv X \text{ or } B)$ electronic state. In a similar spirit to that of Ref. 5, the basis set used to diagonalize H^{Yv} is given by

FIG. 1. Calculated (thick line) and experimental (thin line) parity selected excitation spectra of He_2Cl_2 $B(v'=8) \leftarrow X(v=0)$ band. (a) Transition to final B states symmetric under chlorine exchange. (b) Transition to final B states antisymmetric under chlorine exchange. The rotational temperature in the calculated spectra is 1 K. Experimental data are from Ref. 1. Individual lines are drawn as sticks. The main ones are labeled and their position is given in Table I.

$$\Phi_{(\Omega_1 n_1)(\Omega_2 n_2)}^{Y; JM\Omega}(\hat{r}, \mathbf{R}_1, \mathbf{R}_2) = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{M\Omega}^{J*}(\phi, \theta, 0) \times \psi_{(\Omega_1 n_1)}^Y(\mathbf{R}_1) \psi_{(\Omega_2 n_2)}^Y(\mathbf{R}_2), \quad (2)$$

with the condition $\Omega_1 + \Omega_2 = \Omega$. In Eq. (2), $\mathbf{J} = \mathbf{j} + \mathbf{l}_1 + \mathbf{l}_2$ is the total angular momentum, and M and Ω its projections on the laboratory Z and body-fixed z axes, respectively; Ω_i is the projection quantum number of $\mathbf{l}_i$ on the z axis; $D_{M\Omega}^J$ is a Wigner function; and $\psi_{(\Omega_i n_i)}^Y(\mathbf{R}_i)$ is the n_i^{th} eigenfunction of $\langle \chi_v^Y | H_{\text{Cl}_2-\text{He}} | \chi_v^Y \rangle$, obtained by diagonalization in a product basis set of harmonic oscillator functions times spherical harmonics with projection Ω_i .

A symmetrized basis set was constructed by working out the effect of all the symmetry operators on the basis functions (2): $\hat{\epsilon}$ is the inversion of all the nuclear coordinates, $\hat{\eta}$ is the exchange of the chlorine atoms, and $\hat{\kappa}$ is the exchange of the helium atoms. Each symmetry block of the Hamiltonian matrix H^{Yv} (for the eight combinations of eigenvalues ϵ, η, κ

$= \pm 1$) was diagonalized for $J=0,1,2,3$ in both the X and B electronic states. The energy levels were converged within 0.07 cm^{-1} at worst. More details on the computational procedures will be given in a future publication.

RESULTS AND DISCUSSION

The He_2Cl_2 $B(v'=8) \leftarrow X(v=0)$ absorption spectra were calculated assuming a transition dipole moment μ lying along the Cl-Cl axis (as is the case for the corresponding transition in Cl_2 and in $\text{HeCl}_2^{2,8}$). From the behavior of μ under the symmetry operations of the system: $\hat{\epsilon}(\mu) = -\mu$, $\hat{\eta}(\mu) = -\mu$, $\hat{\kappa}(\mu) = \mu$, the following selection rules are obtained: $\epsilon\epsilon' = -1$, $\eta\eta' = -1$, $\kappa\kappa' = +1$. The selection rule for the total angular momentum is $\Delta J = 0, \pm 1$.

The parity selected spectra were calculated for a rotational temperature of 1 K and a (Lorentzian) homogeneous linewidth of 0.06 cm^{-1} . Figures 1(a) and 1(b) present the $B(\eta' = +1) \leftarrow X(\eta = -1)$ and $B(\eta' = -1) \leftarrow X(\eta = +1)$ tran-

TABLE I. Assignment for the main transitions in He_2Cl_2 $B(v'=8) \leftarrow X(v=0)$ spectra. ν refers to the internal vdW vibrational excitation. The frequency is referred to the $\text{Cl}_2 B(v'=8) \leftarrow X(v=0)$ band origin.

Label	Freq. (cm^{-1})	X		B	
		J_{η}^e	ν	$J_{\eta'}^{e'}$	ν'
$\eta' = +$ [Fig. 1(a)]	a	5.70	3 $^-$ 0	2 $^+$ 0	
	b	5.95	2 $^+$ 1	1 $^-$ 1	
	c	6.33	1 $^-$ 0	0 $^+$ 0	
	d	6.48	2 $^-$ 0	2 $^+$ 0	
	e	6.51	1 $^+$ 1	1 $^-$ 1	
	f	6.86	1 $^+$ 1	2 $^-$ 1	
	g	6.91	1 $^-$ 0	2 $^+$ 0	
	g'	6.92	2 $^+$ 1	3 $^-$ 1	
	h	7.07	2 $^-$ 0	3 $^+$ 0	
$\eta' = -$ [Fig. 1(b)]	i	7.16	1 $^-$ 0	2 $^+$ 0	
	a	5.71	2 $^+$ 0	1 $^-$ 0	
	a'	5.98	2 $^-$ 1	1 $^+$ 1	
	b	6.06	2 $^+$ 0	1 $^-$ 0	
	c	6.31	2 $^+$ 0	2 $^-$ 0	
	d	6.48	1 $^-$ 1	1 $^+$ 1	
	e	6.66	2 $^+$ 0	2 $^-$ 0	
	f	6.86	0 $^+$ 0	1 $^-$ 0	
	g	6.98	2 $^+$ 0	3 $^-$ 0	
	h	6.88	1 $^+$ 1	2 $^+$ 1	
	h'	6.90	2 $^-$ 1	3 $^-$ 1	

sitions, respectively, compared with experiments.¹ It can be seen that the calculated peak positions are very accurately reproduced and the line intensities are also in very good agreement. The main lines contributing to the spectra are shown as sticks, and their assignment is given in Table I. Note that only *symmetric* wave functions under the exchange of He atoms contribute to the spectra, since the nuclear spin of ^4He is zero. For ^3He both symmetric and antisymmetric wave functions will contribute but with different spin statistics.

In order to get more insight into the rovibrational structure of this cluster, the energy levels involved in the spectra for the B state are shown in Fig. 2. A corresponding diagram for the X state, being quite similar, is not presented here. The antisymmetric ($\kappa = -1$) levels under He exchange are depicted with dashed lines and the symmetric ($\kappa = +1$) ones with full lines. Although those antisymmetric states do not exist in this molecule, their inclusion is useful in order to understand the structure of the energy levels. Two "rotational series," displaced by about 0.5 cm^{-1} from each other, are distinguishable in Fig. 2. Both series are overlapping in the spectrum. The upper one is attributed to the first vdW vibrational excitation [in the $\phi_1 - \phi_2$ (He-He) bending coordinate]. The $J=0$ ground van der Waals state is symmetric in both electronic states and has a dissociation energy of 32.19 cm^{-1} for $X(v=0)$ and 25.54 cm^{-1} for $B(v'=8)$. Both dissociation energies are roughly twice the dissociation energies of the HeCl_2 systems,⁸ which is in agreement with previous findings on He_2Cl_2 ⁶ (using a different potential) and He_2I_2 .⁵

We have attempted to fit the energy levels represented in Fig. 2 and the corresponding ones for the X state to the levels of an asymmetric rigid rotor, checking the assignment by working out the behavior of the rigid rotor functions under

FIG. 2. Energy levels diagram for the $B(v'=8)$ states involved in the spectra of Fig. 1, and for total angular momentum $J=0,1,2,3$. Full lines are for states symmetric under He exchange ($\kappa = +1$), whereas dashed lines represent antisymmetric states ($\kappa = -1$). The energy levels are referred to the dissociation limit $\text{Cl}_2(B(v'=8)) + \text{He} + \text{He}$.

the three symmetry operations of the system (this will be detailed in a forthcoming paper). The agreement was better than expected. The energy levels of the ground vdW state (first rotational series) can be reproduced (within $\pm 0.07 \text{ cm}^{-1}$) by a structure in which the He atoms sit in a plane perpendicular to the Cl-Cl axis, with bond lengths very close to those obtained in a rigid rotor fit for the triatomic HeCl_2 ² (chlorine interatomic distances $r_X = 1.99 \text{ \AA}$ and $r_B = 2.64 \text{ \AA}$, and helium to chlorine axis distances $R_X = 3.6 \pm 0.1 \text{ \AA}$ and $R_B = 3.8 \pm 0.1 \text{ \AA}$ for the X and B states, respectively). The angle between the helium atoms was found to lie between 125° and 150° for both electronic states. The large error bars on the coordinates of the He atoms show how little sensitive the constants of inertia are with respect to displacements of the atomic positions. This could explain the apparent contradiction of a floppy molecule with a rigid rotor spectrum. The resulting average distance between helium atoms is nearly $7 \text{ \AA}$, in accordance with the corresponding probability distribution of Ref. 6. For the first vdW excited state (i.e., the second rotational series), a similar structure with a smaller angle between the helium atoms (of about 100°) simulated the sequence of energy levels, although a bit less accurately. The smaller angle can be rationalized in a simplified model for the bending motion [similar to the one proposed in Ref. 11(b)], where the bond lengths are held

fixed (at the rigid structure values) and the helium atoms are constrained to move in a plane perpendicular to the Cl–Cl bond containing its center of mass. The effective potential for the He–He bending angle φ is symmetric with respect to $\varphi=\pi$, with repulsive walls at $\varphi=0$ and at $\varphi=2\pi$ and a barrier at $\varphi=\pi$ separating two minima at $\varphi=\varphi_e$ and $2\pi-\varphi_e$. That potential being very shallow, the zero point level is nearly at the top of the barrier and the corresponding wave function has an important probability density between φ_e and $2\pi-\varphi_e$. The first excited bending level on the other hand has a node at $\varphi=\pi$, hence the average value for $\cos^2 \varphi$ (which is the quantity appearing in the inertia tensor for He_2Cl_2) is smaller.

Apart from the problem of the two overlapping series of levels, the main difficulty in performing a rigid rotor fit to the spectra rests on the exchange symmetry imposed on the spatial wave function by the zero spin of the ^4He . This is inherently a nonrigid property, since one has to look into the structure of the nonrigid Hamiltonian to get the behavior of the He–He bending wave function under He exchange. In a forthcoming paper, it will be shown that the rigid rotor wave function remains unchanged and the bending wave function is multiplied by $(-1)^{p_K+\nu}$, where K is the projection quantum number of J onto the rigid body z axis (the Cl–Cl axis), p_K is the parity (0 for even, 1 for odd) of K of the symmetric rigid rotor functions used to build the asymmetric rotor solutions (see Ref. 12), and ν is the He–He bending level. Since He are zero-spin bosons, the zero-point vdW state ($\nu=0$) can only be associated with rigid rotor functions built with even K , while the first excited vdW state ($\nu=1$) is associated with odd K . For the ^3He cluster all the wave functions are allowed, with a statistical weight $(-1)^{p_K+\nu} = 1: (-1)^{p_K+\nu} = -1$ equal to 1:3.

Finally, it would be very interesting to know to what extent the concept of an average structure still holds for larger clusters, i.e., He_NCl_2 ($N=3,4,\dots$). This question is further motivated by recent experiments using atoms and small molecules for probing very large helium clusters.^{13,14} Very recently, McMahon *et al.* have performed a quantum Monte Carlo study on the effect of rotations in He_7 and $(\text{H}_2)_7$ clusters,¹⁵ finding extreme centrifugal distortions in these clusters as the angular momentum increases. As suggested by Barnett and Whaley,¹⁶ this effect might not be so dramatic in clusters like He_NCl_2 since the stronger interaction between the He atoms and the impurity (Cl_2) would force the He atoms to be more localized (as we find for He_2Cl_2). However, the difficulty for getting an average structure for a cluster like He_NCl_2 from its experimental spectrum is even bigger than for He_2Cl_2 , because of the more complicated exchange effects and the larger number of low frequency He–He bending modes that are excited in the same region.

CONCLUSIONS

We have presented a three-dimensional calculation of the $B(v'=8) \leftarrow X(v=0)$ spectrum of He_2Cl_2 van der Waals molecule. The approach followed here, which assumes additive Cl–Cl, He– Cl_2 , and He–He interactions, has proved to

be very realistic in view of the excellent agreement with the experimental spectra of Janda and co-workers.¹ It has been found that in spite of the extreme floppiness of He_2Cl_2 , the concept of an average geometry for the lowest vdW states is still valid. The difficulty in getting structural parameters from a rigid rotor fit to the experimental spectrum is double: first, two series of levels overlap due to the very low He–He bending frequency, and second, only half of the rigid rotor levels are allowed due to the fact that the ^4He nuclei have zero spin, and that they actually *can* exchange in this floppy system. For ^3He all levels will appear but with different statistical weight. To enhance the understanding of this system (i.e., the effect of floppiness, the adequacy or inadequacy of the rigid rotor model) it would be interesting to know the probability distributions of the different rovibrational states on the different degrees of freedom and study their dependence on the total angular momentum. Work in this direction is currently in progress.

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