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Conformation, structure, quadrupole coupling constants and van der Waals potential energy surface of dichloromethane–Ar

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ABSTRACT

The rotational spectra of the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species of dichloromethane–argon have been investigated by molecular beam Fourier-transform microwave spectroscopy. Information on the configuration, structure and internal dynamics of the complex has been obtained, and the ^{35}Cl and ^{37}Cl quadrupole coupling constants have been determined, based on the experimental data.

1. Introduction

Rotational spectra of molecular adducts of rare gases with small asymmetric molecules are generally characterized by inversion splittings due to the low barriers between equivalent minima in the two-dimensional (2D) potential energy surface of angular motions [1–10]. This is the case, for example, of the complexes of difluoromethane (CH_2F_2) with all rare gas (RG). Inversion splittings of 39.316(1), 79.19(4) and 193.740(1) MHz have been reported for CH_2F_2–Xe [10], CH_2F_2–Kr [9] and CH_2F_2–Ar [8], respectively. For CH_2F_2–Ne the splitting is of the order of 6 GHz, but the spectrum is not yet satisfactorily interpreted [11]. In going from difluoromethane to chlorofluoromethane (CH_2ClF), that is substituting a fluorine with a chlorine atom in the RG partner molecule, one can observe a considerable decrease of the inversion splittings, to 0.1360(2), 0.6298(6) and 2.9219(5) MHz for the most abundant isotopologues of CH_2ClF–Xe [12], CH_2ClF–Kr [13] and CH_2ClF–Ar [14], respectively. Again, the spectrum has not yet satisfactorily assigned for the complex with neon, CH_2ClF–Ne [15].

To better understand the effects of the size and of the electronegativity of the halogen atom on the potential energy surface of the van der Waals motions, we decided to investigate the rotational spectrum of dichloromethane CH_2Cl_2–Ar. For this complex, apart the possible inversion tunneling, the spectrum is expected to be severely complicated by the quadrupole effects of the two Cl atoms, with nuclear spin quantum number $I = 3/2$, for both ^{35}Cl and ^{37}Cl isotopes. A sketch of CH_2Cl_2–Ar is given in Fig. 1, with the principal axis systems and the polar coordinates defining the position of Ar with respect to CH_2Cl_2.

2. Experimental part

The MB-FTMW spectrum in the 6–18.5 GHz frequency region was measured using a COBRA-type [16] pulsed supersonic-jet Fourier-transform microwave (FT-MW) spectrometer [17] described elsewhere [7]. A mixture of 2% CH_2Cl_2 in Ar was expanded from ca 3 bar to about 10^{-5} mbar. Each rotational line is split by Doppler effect, enhanced by the molecular beam expansion in the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz and lines separated by more than 7 kHz are resolvable.

2.1. Plausible conformations of CH_2Cl_2–Ar

Before to search for the rotational spectrum, we ran some model calculations, in order to have a reliable starting conformation. Serving this purpose we utilized first the simple distributed polarizability model (DPM) [18,19], followed by ab initio calculations in the vicinity of the DPM minima.

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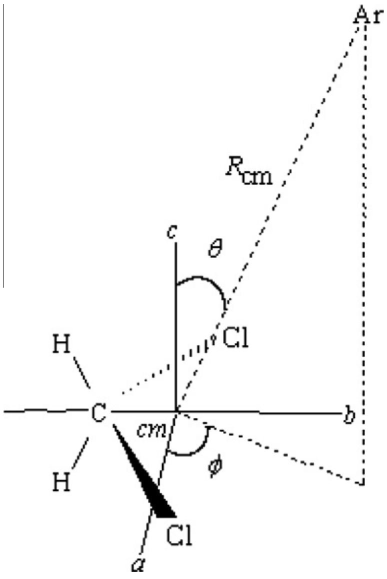

Fig. 1. Sketches of CH_2Cl_2–Ar with the polar coordinates defining the position of Ar with respect to CH_2Cl_2.

(a) *The DPM calculations* were performed using the computer program RGDMIN [20]. The geometry of CH_2Cl_2 was fixed to the experimental r_0 structure [21] while the distance (R_{CM}) between its center of mass (CM) and the rare gas was free to relax for energy minimization in the full range $\theta = 0$–$180°$, $\phi = -90$–$270°$ at steps of $\Delta\phi = \Delta\theta = 15°$. R_{CM}, θ and ϕ are the spherical coordinates shown in Fig. 1. The obtained two-dimensional (2D) potential energy surface is shown in Fig. 2. It is qualitatively quite similar to that found for CH_2F_2–Ar [8], with two main equivalent minima.

(b) *Ab initio optimizations* at the MP2/6-311++G(d, p) level of theory were performed with the Gaussian03 suite of programs [22] on the found doubly degenerate minimum. These calculations were also useful to calculate the set of quadrupole coupling constants (χ_{hg}, $h, g = a, b, c$). The ab initio calculations suggested, with respect to the DPM configuration, a considerable shift of the Ar atom towards the carbon atom. In Table 1, we report the DPM and MP2/6-311++G(d, p) geometries, the calculated values for the rotational and quadrupole coupling constants, and for the R_{cm} and θ structural parameters (ϕ is 90° in both cases). In the case of the DPM configuration, the quadrupole coupling constants have been calculated at the MP2/6-311++G(d, p) level, but keeping the geometry fixed at the DPM value.

2.2. Rotational spectrum

The search of the spectrum was based on the rotational constants calculated for the geometries obtained with both theoretical approaches and using the quadrupole coupling constants provided in Table 1. We assigned first the set of μ_c-type transitions $(J+1)_{1J}$–J_{0J}, with J in the range from 2 to 4. Their frequencies were much closer to the values calculated with the DPM model. All of them showed a complex hyperfine structure as, for example, that of the 4_{13}–3_{03} transition in Fig. 3. Then, many more μ_c-type transitions have been measured, for a total of 144 component lines. None of them displayed a tunneling splitting.

All measured line frequencies are reported as Supporting Information. These frequencies have been fitted with a Pickett SPFIT computer program [23], according to the Hamiltonian:

$$\mathbf{H} = \mathbf{H}_R + \mathbf{H}_{CD} + \mathbf{H}_Q \qquad (1)$$

where $\mathbf{H}_R$, $\mathbf{H}_{CD}$ and $\mathbf{H}_Q$ are the rotational, centrifugal distortion and quadrupolar interaction contributions, respectively.

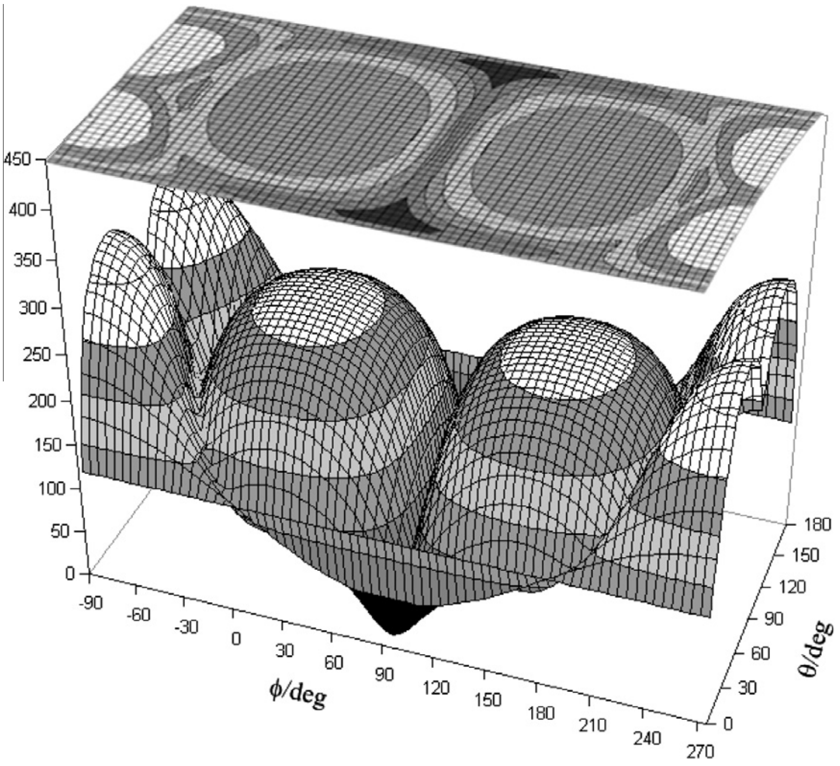

Fig. 2. Distributed polarizability model calculations: two- and three-dimensional potential energy surface as a function of the spherical coordinates θ and ϕ.