Helium Atom Scattering from Cyclopentane, Pyrrolidine and Tetrahydrofurane in Crossed Molecular Beams

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Scattering of helium atoms by cyclopentane, pyrrolidine and tetrahydrofurane molecules was observed in crossed molecular beam experiments. The intensity of scattered helium atoms, depending on the scattering angle, was measured with high resolution, and the damping of the diffraction oscillations of the differential cross sections was used to extract elastic anisotropic interaction potentials for these molecules. The evaluation included a geometric transformation concerning the puckered states of the envelope and the twisted conformation of the molecules. The potentials were found to be rather similar.

Key words: Molecular beams, helium, saturated 5-rings, interaction potentials, ring puckering

1. Introduction

The shape of intermolecular interactional potentials can be extracted from rotationally unresolved total differential cross sections (DCS) as measured by He atom scattering even for rather anisotropic molecules [1 - 3]. In the present work, scattering experiments were carried out with five-membered saturated rings such as cyclopentane (C_5H_{10}), pyrrolidine (C_4H_8NH) and tetrahydrofurane (C_4H_8O) [4]. To obtain the intermolecular potentials, results from an infinite order sudden approximation (IOSA) [5 - 8] were fitted to experimental DCS data resulting from crossed molecuar beam experiments. Modified and anisotropically expanded Hartree Fock dispersion potentials (HFD) [9] were chosen for computational modelling of the interactions.

2. Experimental

The main experimental configuration has already been described in detail [1, 2, 10]. Fixed and well collimated supersonic nozzle beams of He (primary beam) and the respective molecules (secondary beam) were crossed rectangularly. Since the scattering molecules in the present case are more complex, the He beam source had to be improved in order to increase the experimental resolution [11, 12]. Beam orientations were precisely adjusted using laser tubes to achieve suitable orthogonality. Collimation and velocity spread of either beam was optimized and controlled repeatedly with beam profile measurements and time-of-flight (TOF) analysis. Furthermore the equipment and procedure was tested and verified by measuring of the He-Ar DCS, which are very well known [13 - 16].

A quadrupole mass filter (Type 329-9, Extranuclear, USA) and a channeltron detector (Type 4816, Galileo, Sturbridge, USA), separately enclosed in a UHV chamber, could be rotated in-plane (with respect to both beams) around the scattering center.

The beam of the scattering molecules was produced from a "liquid" source as described in [17]. Beam conditions and some characterizing data for the improved experimental equipment are given in Table 1. For the "organic" beams the speedratio was found almost constant for a source pressure up to 200 mbar. This indicates that cluster formation is negligible below this pressure [11]. For the scattering experiments, the secondary source was operated with a pressure of only 100 mbar.

Experimental DCS curves are shown in Fig. 1; DCS data are given in Table 2 and may be used with any

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Table 1. Beam conditions.

	He	C_5H_{10}	C_4H_8NH	C_4H_8O
Gas purity (%)	99.996	>99	>99	>99
Source pressure (bar)	45	0.1	0.1	0.1
Bath temperature of liquid source (K)	—	273	288	285
Nozzle temperature (K)	303	350	353	358
Nozzle diameter (μm)	20	100	100	100
Skimmer diameter (mm)	0.3	0.5	0.5	0.5
Nozzle-skimmer distance (mm)	20	2.0	2.0	2.0
Bath temperature of	—	273	288	285
Collimator diameter (mm)	1.0	—	—	—
Most probable velocity (ms^{-1})	1625	714	705	680
Angular divergence (degree)	0.9	7.0	6.7	7.0
Speed ratio S	40	5.2	4.8	5.5
Collision energy (meV)	—	61.9	61.5	60.9

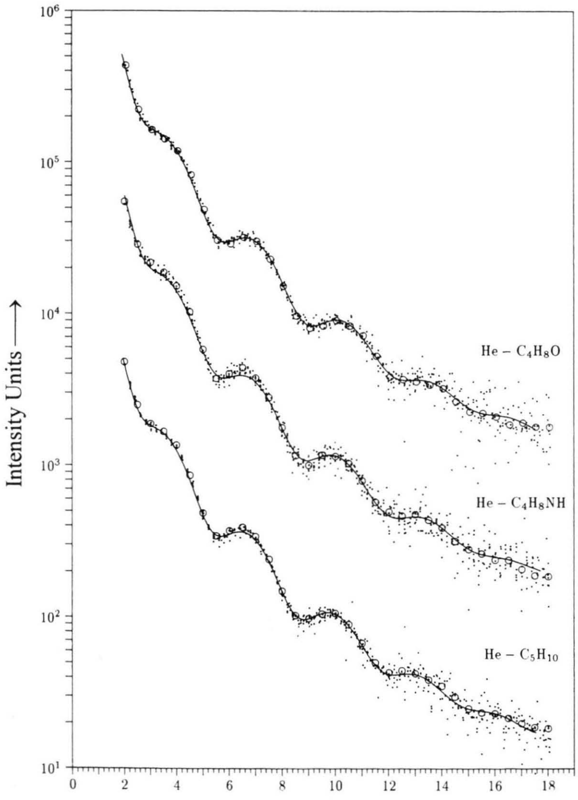

Fig. 1. Laboratory differential cross sections for the scattering of He by C_5H_{10}, C_4H_8NH and C_4H_8O. The ordinates are shifted arbitrarily. Small dots are experimental measurements of the total differential cross section, open circles are smoothed mean values. Solid lines are calculated using best-fit potentials extracted from measured data.

Table 2. Experimental total differential cross section measurements.

Θ	HeC_5H_{10}	HeC_4H_8NH	HeC_4H_8O
2.00	10000.0	10000.0	10000.0
2.50	5194.7	5194.8	5086.5
3.00	3889.1	3939.6	3747.3
3.50	3455.0	3411.1	3257.8
4.00	2804.0	2756.4	2715.1
4.50	1784.1	1861.6	1886.5
5.00	1005.1	1049.9	1110.0
5.50	710.6	674.7	696.6
6.00	766.7	725.2	662.8
6.50	811.8	798.4	728.0
7.00	704.2	681.7	687.7
7.50	498.0	506.8	522.5
8.00	306.8	320.5	347.5
8.50	212.6	209.3	221.2
9.00	203.9	180.6	183.3
9.50	217.4	211.3	189.9
10.00	220.1	207.9	206.8
10.50	184.8	186.6	189.8
11.00	140.1	143.2	163.5
11.50	104.3	103.6	119.8
12.00	89.8	89.9	87.8
12.50	92.3	84.3	83.9
13.00	88.5	86.5	81.2
13.50	79.9	79.0	77.6
14.00	72.9	70.3	73.5
14.50	61.9	57.4	60.2
15.00	51.8	50.7	51.3
15.50	48.8	47.3	50.4
16.00	48.2	43.2	47.8
16.50	44.8	43.0	42.3
17.00	41.4	37.6	43.7
17.50	39.0	34.0	40.8
18.00	38.6	33.7	41.0

potential model. In order to achieve satisfying signal to noise ratio, the complete set of data for each curve was measured repeatedly up to ten times.

3. Potential Model and Procedure

The experimental results were analyzed by means of the infinite order sudden approximation (IOSA) [18]. This method was found valid in the case of He-C_6H_6 scattering for similar conditions [1]. Thus the IOSA should be valid also in the present case, since the rotational characteristica are sufficiently similar.

Calculations were based upon a modified form of the HFD potential of Aziz et al. [15], which is one of the potentials mainly used [9], since its parameters are physically more meaningfull. For the isotropic part of the interaction potential we used

$$V(R) = \varepsilon_m F(r), \tag{1}$$

$$r = \frac{R}{R_m}, \tag{2}$$

$$F(r) = F_{rep}(r) + F_{att}(r)d(r), \tag{3}$$

$$F_{rep}(r) = a \exp\left[-b(r-1)\right], \tag{4}$$

$$F_{att}(r) = -\left(\frac{c_6}{r^6} + \frac{c_8}{r^8} + \frac{c_{10}}{r^{10}}\right), \tag{5}$$

$$d(r) = \begin{cases} e^{-\left(\frac{1.28}{r}-1\right)^2} & \text{for} \quad r \leq 1.28 \\ 1 & \text{for} \quad r > 1.28 \end{cases} . \tag{6}$$

ε_m and R_m are the energy parameter and range (or distance) parameter of the potential. The van-der-Waals coefficients c_6, c_8 and c_{10} describe dipole-dipole, dipole-quadrupole and quadrupol-quadrupole interaction, respectively. The coefficients c_n and a were used in their reduced form

$$c_n = \frac{C_n}{R_m^n \varepsilon_m}, \tag{7}$$

$$a = \frac{A}{\varepsilon_m}. \tag{8}$$

c_{10} was taken to be [19]

$$c_{10} \approx 1.225 \frac{c_8^2}{c_6}. \tag{9}$$

The parameters a and b of (4) were calculated from the minimum conditions of the respective potential:

$$\frac{\mathrm{d}F(r)}{\mathrm{d}r} = 0, \tag{10}$$

$$F(1) = -1. \tag{11}$$

As previously [1, 2] the anisotropy of the scattering molecule may be taken into account by expanding the energy and range parameters, ε_m and R_m, into Legendre polynomials or spherical harmonics corresponding to the symmetry of the molecules:

$$R_m = \sum_i R_i Y_{ij}, \tag{12}$$

$$\varepsilon_m = \sum_i \varepsilon_i Y_{ij}. \tag{13}$$

Table 3. Interactional potential parameters of He – XH_n scattering systems.

	ε_m meV	R_m pm	Ref.	Method
He - CH_4	2.25	3.78	[2]	crossed molecular beam scattering
He - NH_3	2.28	3.60	[27]	crossed molecular beam scattering
He - OH_2	2.40	3.38	[28]	ab initio SCF calculation

Although some contribution of anisotropy is due to the hetero atoms of pyrrolidine and tetrahydrofurane, the symmetry in the present case was primarily assumed to be $D_{\infty h}$. This assumption may be justified from the fact that the differences of the energy and range parameters for the prototypic scattering systems He-CH_4, He-NH_3 and He-OH_2 are quite small (Table 3). Also, taking into account some kind of bulge with respect to the fivefold molecular axis no satisfying solution could be found within an acceptable range of parameter variations for pyrrolidine and tetrahydrofurane. According to the assumed basic symmetry $D_{\infty h}$ merely the spherical harmonics

$$Y_{00} = 1 \tag{14}$$

and

$$Y_{20} = \frac{3\cos^2\vartheta - 1}{2} \tag{15}$$

were used.

Pitzer strain distorts the 5-ring molecules into one of two different conformations [20, 21], called *envelope* and *twisted* (or *halfchair*) (see Figure 2). Since the energy barrier between these conformational states is low, the molecules easily change from one state to the other in some kind of pseudorotation. Any modelling of the puckered geometry would be troublesome when using combinations of spherical harmonics. Therefore a transformation function

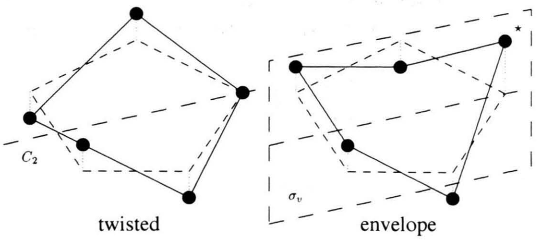

Fig. 2. The two conformations of the saturated five-membered ring molecules.

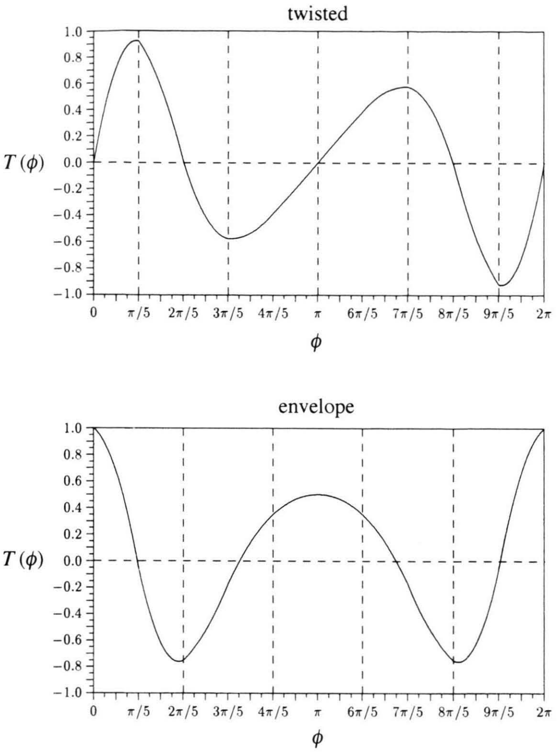

Fig. 3. The longitudinal terms of the geometrical transformations.

was introduced [4] which deforms the $D_{\infty h}$ oblate molecular shape into a puckered Pitzer model:

$$R_m(\vartheta, \phi) = R_0 Y_{00}(\vartheta_t, \phi) + R_2 Y_{20}(\vartheta_t, \phi) \;, \quad (16)$$

$$\varepsilon_m(\vartheta, \phi) = \varepsilon_0 Y_{00}(\vartheta_t, \phi) + \varepsilon_2 Y_{20}(\vartheta_t, \phi) \;. \quad (17)$$

The azimutal polar angle ϑ is distorted depending upon the longitudinal angle ϕ:

$$\vartheta_t = \vartheta - f \sin(\vartheta) T(\phi) \;, \quad (18)$$

f is an adjustable scale factor. In the case of the twisted conformation $T(\phi)$ is given by (see Figure 3)

$$T(\phi) = \frac{\sin(\phi + \frac{\sin\phi}{2}) + 3 \sin 2(\phi + \frac{\sin\phi}{2})}{4} \;, \quad (19)$$

and in the case of the envelope conformation

$$T(\phi) = \frac{\cos(\phi + \frac{\sin\phi}{2}) + 3 \cos 2(\phi + \frac{\sin\phi}{2})}{4} \;. \quad (20)$$

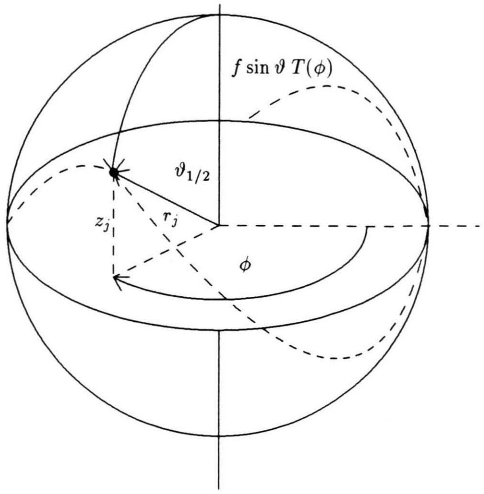

Fig. 4. Description of the molecules in polar coordinates.

$\sin(\vartheta)$ causes strongest distortion with respect to the equatorial plane, while the poles of the molecules remain undistorted. The transformation is unequivocal as long as $|f| \lesssim 1$.

A relation can be found between f and the puckering amplitude q from Pitzer's equation [20, 21]. Let $\vartheta_{1/2}$ be that angle ϑ transformed to the equatorial plane ($\vartheta_t = \pi/2$):

$$\pi/2 = \vartheta_{1/2} - f \sin(\vartheta_{1/2}) T(\phi) \quad (21)$$

(see Figure 4). If f and $T(\phi)$ are given, $\vartheta_{1/2}$ can be calculated iteratively. Now let z_j be the displacement of the carbon atom j perpendicular to the plane of the unpuckered ring [20]. If r_j is the distance between the atom and the geometrical center of the molecule, then

$$z_j = r_j \sin(\frac{\pi}{2} - \vartheta_{1/2}) \;. \quad (22)$$

For the atom marked with an asterisk ($\star$) in Fig. 2 (envelope, $\phi = 0$), according to Pitzer's equation $z_\star$ is

$$z_\star = q\sqrt{\frac{2}{5}} \;, \quad (23)$$

where q is the puckering amplitude. With (22) follows

$$q = \sqrt{\frac{5}{2}}\, r_\star \sin(\frac{\pi}{2} - \vartheta_{1/2}) \;. \quad (24)$$

Note that in this specific case the determination of $\vartheta_{1/2}$ by (21) is simple, since $T(\phi) = 1$.

Certainly the transformation of a $D_{\infty h}$ oblate shape is a drastic simplification. But including all possibilities there are 11 different conformations of the puckered pyrrolidine molecule, due to the nitrogen atom with its lone pair electrons pointing out to one side, and a bound hydrogen atom sticking out to the other side of the puckered ring. There are six conformations for tetrahydrofurane and two for cyclopentane. Calcultions including all conformational contributions to the DCS would have been not only beyond the frame of our computational resources but supposedly also out of the limits of experimental resolution.

The potential parameters and the scale parameter, f, of the transformation were determined by least square fitting of calculated DCS into the experimental data. The DCS were computed first in the center of mass system for various orientations of collision [5, 22]. Computation was performed by means of partial wave analysis whith phase shifts which were calculated from the JWKB approximation with Langer's modification [23]. The DCS results were then transformed into the laboratory system, using the elastic Jacobian. The DCS in the laboratory system were averaged with respect to angular and velocity spread of either beam and to the finite aperture of the detector. A more detailed description of the data analysis and the fitting procedure is given in [1, 2, 10].

Results and Discussion

Best fit potential parameters are given in Table 4. The ε_i describe the well depth of the energy. R_i are the corresponding distance parameters according to (2). As mentioned, the van-der-Waals coefficients c_6, c_8 and c_{10} describe the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. f is the scaling factor of (18). For the envelope and the twisted form of either of the three scattering systems the potential parameters turned out to be equal. Therefore just one set of parameters is given for either system.

The uncertainties given in Table 4 have been obtained from the fit calculations by varying the data of the apparative condition parameters within the limits of tolerance [4]. The potential parameters of the three systems under investigation are found quite similar, except ε_2 and f. These coefficients are mainly responsible for the interaction anisotropy. One may expect some trend from cyclopentane to tetrahydrofurane, due to the chemical and pysical properties of the C, N and O atoms. The discrepancy found might be attributed to the neglection of heterogenity, as mentioned in the previous section. Concerning the (isotropic) dispersion coefficients, c_n, there is some trend to enhanced dipole-dipole interaction from cyclopentane to tetrahydrofurane which corresponds to the growing dipole moment. The average well depth ε_0 is almost twice that of He-CH_4 [2]. This is certainly due to the fact that the 5-ring molecules are larger and thus have greater polarizabilities.

Table 4. Best-fit potential parameters.

Paramter	HeC_5H_{10}	HeC_4H_8NH	HeC_4H_8O	Uncertainty
ε_0 (meV)	4.62	4.51	4.60	0.3
ε_2 (meV)	1.59	3.39	2.27	0.3
R_0 (pm)	454	463	440	15
R_2 (pm)	-61	-60	-63	4
a	0.719	0.798	0.634	—
b	16.42	15.10	16.41	—
c_6	1.122	1.267	1.333	0.1
c_8	0.483	0.467	0.333	0.1
c_{10}	0.255	0.211	0.102	0.05
f	0.283	0.153	0.223	0.04

Results are shown graphically in Figure 5. The interaction energy is plotted versus the central distance. An approach of helium atoms perpendicular (⊥) to the "equatorial plane" causes the interaction to be

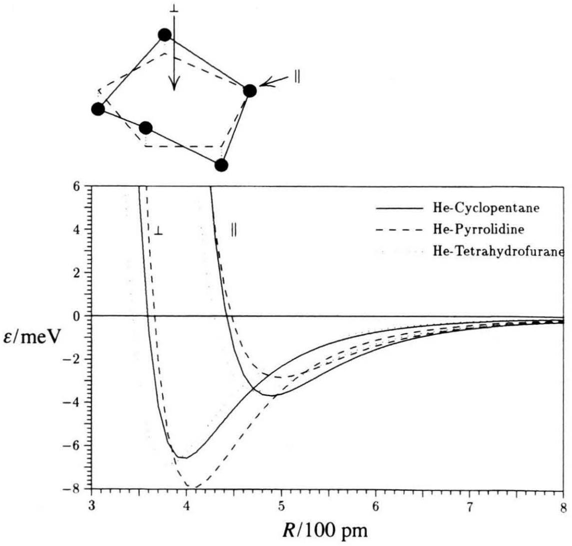

Fig. 5. Potential plots in case of "perpendicular" resp. "parallel" approach.

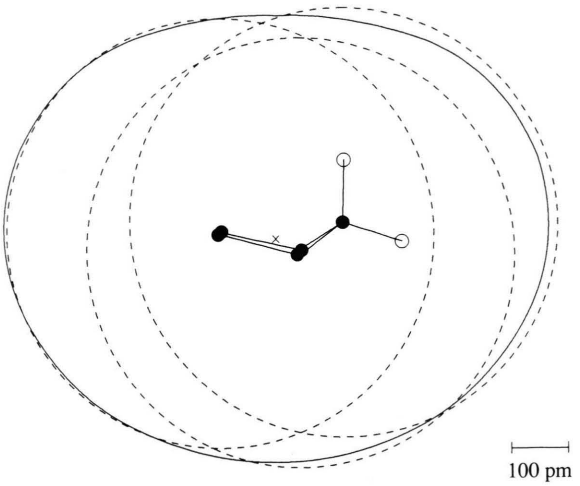

Fig. 6. Section through the helium-cyclopentane interactional potential.

more attractive than an in-plane (||) approach. This is similar to the helium interactions found for the respective aromatic molecules [12], although in the present case no aromatic π electron system can be used for explanation. But when approaching perpendicularly, helium atoms may interact simultaneously with several different locations of the mainly oblate molecule, while approaching in-plane appreciable interaction will concern only some molecular sector.

Figure 6 presents a section, cut in the mirror plane, through the He-C_5H_{10} (envelope) interactional shape. The geometric center of the molecule is marked by $\times$. Note that the geometry of the interactional shape turned out to be very close to that of a hypothetical molecule simply assembled from five methane molecules. Filled (single and double) circles represent the carbon nuclei above, in and below the plane. Open circles stand for the two hydrogen nuclei placed in the plane, the other hydrogen nuclei have been omitted. The representation of the molecule is computed from a puckering amplitude $q = 47$ pm [24], bond lengths C–C = 154.6 pm and C–H = 111.3 pm, and bond angle H–C–H = 106° [25]. The dashed circles represent the equilibrium distances of He-CH_4 interaction potential shapes [2], centered upon the carbon nuclei positions of cyclopentane. The solid line shows the R_m parameter of He-C_5H_{10}.

Table 5. Comparison of some puckering amplitude values.

q/pm	Ref.	Method
48	[21]	spectroscopy and thermodynamic calculations
47	[24]	Raman spectroscopy
43.8	[26]	electron diffraction
50 ± 7	this work	crossed molecular beams

Since the scaling factor f, (18), is calculated in the fitting procedure it can be used to calculate the puckering amplitude q according to (21) and (24). Values of q have been determined for cyclopentane by various experimental as well as computational methods; e.g. [21, 24, 26]. The puckering amplitude of the present scattering investigation is found in good agreement with these results (Table 5).

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