

Accurate van der Waals coefficients from absolute total cross sections for the Ar–noble gas systems

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Accurate van der Waals coefficients from absolute total cross sections for the Ar–noble gas systems

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Accurate information on the long range attractive forces due to the induced dipole–induced dipole interaction (and the higher order multipole terms) of ground state atoms is still lacking. Both experiments and theory have failed in providing this information. The absolute value of the total cross section Q and both the shape and magnitude of the small angle differential cross section $\sigma(\theta)$ are very sensitive to this range of the potential. However, very few accurate results for Q are available, as shown in a recent inventory by van den Biesen¹ for the noble gas systems. Typical error bars are 3% to 7% in Q , resulting in errors in C_6 of 7.5% and larger. All measurements have been performed with the conventional technique of calibration of the product of number density and scattering length of a gas cell. Theoretical calculations² of C_6 typically result in upper and lower bounds that differ by 10% (i. e., an error bar of 5%). For this reason, in most potentials proposed, for example the noble gas systems, theoretical values for C_6 , C_8 , and C_{10} are used.

For the measurement of absolute values of the total cross section we have developed two new techniques.³ Method I is based on the absolute calibration of the density–length product $\langle nl \rangle_{\text{ideal}}$ of an undisturbed supersonic secondary beam in a 20 K cryoexpansion chamber,⁴ as given by

$$\langle nl \rangle_{\text{ideal}} = [I(0)/u]G_s, \quad (1)$$

with $I(0)$ ($\text{s}^{-1} \text{sr}^{-1}$) the center line intensity, u the flow velocity, and the function G_s determined by the skimmer geometry. For the case of a slit skimmer perpendicular to the primary beam, G_s can easily be calculated. The expansion will be slightly disturbed by collisions with particles that are backscattered from the 300 K skimmer. This effect is eliminated by the following procedure. By choosing a suitable reference potential we can deconvolute the measured primary beam attenuation and derive $\langle nlQ \rangle_{\text{expt}}$. We define a parameter β as

$$\beta = \langle nlQ \rangle_{\text{expt}} / \langle nl \rangle_{\text{ideal}} Q_{\text{ref}}, \quad (2)$$

with Q_{ref} calculated with the same reference potential. We now write

$$\beta = \beta_Q (1 - F_s \dot{N}), \quad (3)$$

because in first order the attenuation of the secondary beam is proportional to the flow rate \dot{N} through the nozzle. The parameter F_s depends on the specific skimmer geometry, the secondary beam gas, and the nozzle–skimmer distance. The parameter

$$\beta_Q = Q_{\text{expt}} / Q_{\text{ref}} \quad (4)$$

is the so-called Q -comparison factor and can be determined by measuring β as a function of the flow rate \dot{N} ,

with extrapolation to $\dot{N} = 0$ corresponding to an undisturbed expansion.

At this stage of the research the systematic error in the Q -comparison factors β_Q is 1.4%, determined mainly by the systematic error in the calibration of the center-line intensity $I(0)$ by comparison with an effusive source. Random errors in β_Q typically amount to 0.4%. Using two fully different skimmer geometries we find consistent results. Essential for this method is detailed and accurate knowledge of supersonic expansions.⁵

In method II the absolute value of Q is derived from a semiclassical analysis of simultaneous, relative measurements of the total cross section Q and the differential cross section $\sigma(\theta)$ for very small angles $\theta \leq \theta_0$, with θ_0 the quantum mechanical scaling angle. The ratio of the differentially scattered intensity $S_1(\theta)$ and the attenuated primary beam intensity S_2 is in first order independent from the density–length product of the secondary beam. By inserting the dimensions of the scattering experiment and using a suitable reference potential to deconvolute the measurements for the finite angular⁶ and velocity resolution and multiple scattering,⁷ we can derive $\sigma(\theta)/Q$ from the ratio S_1/S_2 . Both the extrapolated value $\sigma(0)/Q$ and the shape of $\sigma(\theta)/Q$ give information on the absolute value of Q . The specific scheme used for the analysis of the data depends on the experimental angular range. Measurements for the system CsF–Ar⁸ have resulted in an accuracy of 1.2%. For the noncondensable gases the signal-to-background ratio is a large problem and the results for Ar–Ar and Ar–Kr still have a rather limited accuracy of 5%. Essential for this method is detailed insight in the processes of small angle scattering.^{6,7,9}

Experimental results for β_Q for Ar–Ar are given in Table I. Within their error bars the previous measurements by Scott, Rothe, and Nenner coincide with our re-

TABLE I. Experimental values for the Q -comparison factor β_Q for the system Ar–Ar in comparison with previous measurements, using the Barker–Fisher–Watts potential as a reference.

Source	g (m s^{-1})	$\beta_Q = Q_{\text{expt}}/Q_{\text{ref}}$
Method I	889	0.965 ± 0.015
Method II	1000	0.970 ± 0.043
Scott ^a	745	0.98 ± 0.04
Rothe ^a	745	0.95 ± 0.07
Nenner ^a	745	0.99 ± 0.02 (?)

^aValues summarized by Van den Biesen and Van den Meijdenberg (Ref. 1).

TABLE II. Experimental C_6 values, in comparison with the calculations of Tang. Only the random errors are given. The systematic error in C_6^{exp} is 3.5% for all systems, based on the 1.4% systematic error in β_Q .

System	Reference potential	C_6^{exp} (10^{-78} J m $^{-6}$)	C_6^{Tang} (10^{-78} J m $^{-6}$)
Ar-Ar	HFDC	5.55 ± 0.03	6.09–6.77
Ar-Kr	BHPS	9.12 ± 0.07	8.48–9.56
Ar-Xe	Schafer	13.43 ± 0.11	11.86–12.81

sults. This also holds for the systems Ar-Kr and Ar-Xe.

To derive an improved C_6 value we use accurate relative measurements of the glory undulations to separate the attractive contribution Q_a^{exp} from the measured Q^{exp} values. The results are given in Table II. For Ar-Ar the C_6 value is significantly lower than predicted by Tang,² for Ar-Kr it is within the theoretical bounds, and for Ar-Xe it is significantly larger than predicted by theory.

Using our experimental results, the attractive branch

of the existing potentials will have to be adjusted rather drastically and a new multiproperty analysis of all existing transport and scattering data is necessary for the Ar-noble gas systems.

Improvements on the signal-to-noise ratio in method II are planned, with the aim to obtain the same accuracy as in method I. Each method can then serve as an independent check on the other method used, which is the final aim of our research program on absolute Q values.

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Dynamical effects on conformational isomerization of cyclohexane

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We report the main result of our NMR study of the pressure effects (up to 5 kbar) on the isomerization rate of cyclohexane in three solvents: acetone- d_6 , carbon disulfide, and methylcyclohexane- d_{14} . A large number of studies¹⁻¹² employing different NMR techniques have been devoted to the investigation of the temperature dependence of the ring inversion of cyclohexane. This is not surprising in view of the fact that the problem of cyclohexane inversion represents the seminal problem in conformational analysis. What is surprising, however, is that all reported studies used a single solvent, carbon disulfide, and that only a limited pressure study (up to 2 kbar) of cyclohexane in a complex mixture of solvents has been performed by Lüdemann and co-workers.¹³

There were two main motivations for our experiments. First, we wanted to investigate the effects of pressure on the isomerization rate of cyclohexane in several solvents. Secondly, in view of recent theoretical activity in the area of stochastic models for isomerization reactions as proposed by Skinner and Wolyones¹⁴ and Montgomery, Chandler, and Berne¹⁵ we attempted to provide the experimental proof of the theo-

retical predictions of these models.

In order to understand the significance of our experimental results one has to mention the main feature of the stochastic models for the isomerization dynamics (for details see the original papers¹⁴⁻¹⁶). In these models it is proposed that there are dynamical effects on isomerization because the reaction coordinate is coupled to the surrounding medium. This leads to the dependence of the transmission coefficient κ upon the so called "collision frequency" α , which in the absence of electrostatic effects reflects the actual coupling of the reaction coordinate to the surrounding medium. In classical transition state theory (TST) κ is assumed to be unity and independent of the thermodynamic state. The stochastic models introduced κ as

$$k(\Delta t) = \kappa k_{\text{TST}}, \quad (1)$$

where $k(\Delta t)$ is the observed isomerization rate and k_{TST} represents the rate as defined in the classical transition state theory. Then it follows that

$$\Delta V_{\text{OBS}}^{\ddagger} = \Delta V_{\text{COLL}}^{\ddagger} + \Delta V_{\text{TST}}^{\ddagger}, \quad (2)$$

where $\Delta V_{\text{OBS}}^{\ddagger}$ is the observed activation volume, $\Delta V_{\text{COLL}}^{\ddagger}$