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METHANE–RARE GAS INTERACTION POTENTIALS FROM SCATTERING EXPERIMENTS

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By using total differential cross sections with resolved diffraction oscillations and absolute integral cross sections with glory oscillations, a new improved spherically averaged potential surface for Ne–CH₄ is determined with a potential well depth of $\epsilon = 5.50$ meV and a minimum distance of $R_m = 3.78$ Å. A slightly improved parameter set is also given for the isotropic Ar–CH₄ interaction. By assuming the same realistic reduced potential form as was found for Ne–CH₄ and Ar–CH₄, the isotropic parts of the potential for Kr–CH₄ and Xe–CH₄ are obtained from absolute integral cross sections.

1. Introduction

Molecular beam scattering experiments have successfully contributed to our precise knowledge of the interaction potentials between the colliding atoms and molecules [1]. In general, integral and total differential cross sections without selection are mainly sensitive to the isotropic part of the potential [2,3], whereas rotationally inelastic collisions provide the most detailed information on the anisotropy of the interaction [4].

Among the polyatomic molecules, the methane–rare gas interactions have attracted much interest in recent years. For the lighter systems He–CH₄ [5] and Ne–CH₄ [6] full potential surfaces were derived using the diffraction oscillations of the total differential cross sections, the angular dependence of rotationally inelastic cross sections, and accurate SCF calculations with damped dispersion forces as input information. Most of the experimental data were well reproduced by a coupled-states (CS) calculation using the resulting potential, but discrepancies concerning the isotropic well depth of Ne–CH₄ and some inelastic transitions remained. Similar results were

obtained for Ar–CH₄ by analysing the elastic rainbow scattering [7] and energy loss spectra [8] using a Morse–spline–van der Waals (MSV) model potential. Very recently total differential cross sections for CH₄–Ne and CH₄–Ar [9] and absolute integral cross section for CH₄–Ne, CH₄–Ar, CH₄–Kr and CH₄–Xe [10] were measured.

The isotropic potentials determined by the differential cross sections [9] using a one-channel elastic calculation are, within the experimental errors, in good agreement with the previous Ar–CH₄ potential [7], whereas, for Ne–CH₄, the well depth ϵ and the minimum distance R_m of ref. [9] (5.69 meV and 3.68 Å) differ appreciably from the values of the complete potential surface of ref. [6] (4.80 meV and 3.83 Å). This is especially intriguing since the R_m values of refs. [9,6] are derived from the same experimental quantity, the positions of the diffraction oscillations which should allow a very precise determination of R_m . The comparison of the measured integral cross sections with the calculated glory oscillations [10] based on the potential of refs. [6,7] shows that for Ar–CH₄ a satisfactory agreement is obtained, considering the experimental uncertainty involved, while for Ne–

CH₄, the product ϵR_m of the potential of ref. [6] is too small.

It is the purpose of this paper, first, to remove this discrepancy for the isotropic Ne-CH₄ potential by using the total differential cross section and the absolute integral cross section simultaneously to determine a model potential of the MSV type. The analysis shows that, for the calculation of the diffraction oscillations, it is not sufficient to use the one-channel (elastic) approximation in contrast to the rainbow and glory scattering for which the contribution of the coupled channel calculation based on the full anisotropic potential to the total cross section is negligible [7,10]. By a similar procedure the isotropic Ar-CH₄ potential is slightly improved compared with the published results [7]. Once reliable potentials are obtained for Ne-CH₄ and Ar-CH₄, these results are used to fix the potential form and to derive reliable size parameters for the heavier rare gas-methane systems Kr-CH₄ and Xe-CH₄ by analysing the absolute integral cross sections. In this way, the whole series from Ne through Xe-CH₄ is covered.

2. The methane-neon system

The complete potential surface for Ne-CH₄ was determined by combining accurate SCF calculations and the known dispersion contribution with measurements of differential energy loss spectra and the diffraction oscillations of the total differential cross sections [6]. By adjusting the damping function of the dispersion to reproduce the experimental data a reliable potential is obtained, since the anisotropy is probed by the rotationally inelastic energy loss spectra and the position of the repulsive wall of the isotropic potential is derived from the diffraction oscillations. This Hartree-Fock-dispersion (HFD) model has the advantage of having built in the correct asymptotic behaviour of the potential, but it contains only one adjustable parameter which makes it somewhat inflexible. The comparison of calculations carried out in the quantum coupled channel approximation with the total differential cross sections is shown in fig. 1a by the solid line. The positions of the oscillations are well reproduced, but the fall-off is too steep indicating a too shallow well. The potential parameters ϵ and R_m are given in table 1 together with

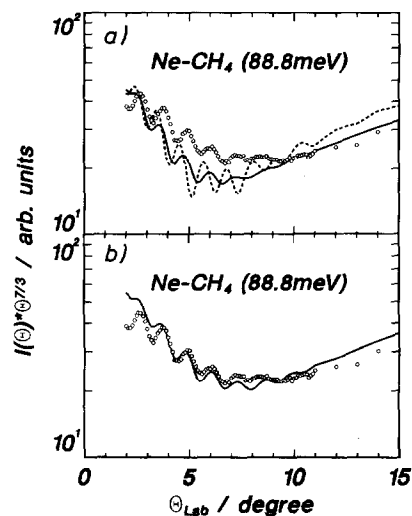


Fig. 1. Measured total differential cross sections for Ne-CH₄ multiplied by $\theta^{2/3}$ in the laboratory system. (a) The solid line is a CS calculation based on the anisotropic potential surface of ref. [6]. The dashed line is in one-channel, elastic calculation based on the spherically averaged potential of ref. [6]. (b) The solid line is a CS calculation based on the spherically averaged MSV potential reported in the text and the anisotropic part of the potential of ref. [6].

the results of ref. [9] (Caltec). The latter potential which is based on the analysis of total differential cross sections, shows a deeper well and disagrees in R_m by 4%, which is surprising considering the sensitivity and the precision of both data sets. However, in the Caltec case, only one-channel (elastic) calculations have been carried out. In order to test the influence of such a calculation on diffractive scattering, we performed a one-channel calculation using the isotropic part of the full potential surface published in ref. [6]. The result is also shown in fig. 1a as a dashed line. The comparison of the two calculations clearly demonstrates that, in the CS calculation, the oscillations are shifted in position and damped so that an evaluation of the experimental data by a one-channel calculation is not adequate leading to too small R_m values. Indeed if we use a model potential of the MSV type [7,9] and fit our data by an elastic calculation, the minimum parameters are $R_m = 3.60$ Å and $\epsilon = 6.50$ meV, which are much closer to the Caltec values. We conclude that for a precise evaluation of diffraction oscillations in the total differential cross section a coupled channel calculation is neces-

Table 1
 ϵ and R_m potential parameters for the isotropic Ne–CH₄ interaction

Reference	Data	Calculation	ϵ (meV)	R_m (Å)
Göttingen [6]	total differential	coupled channel	4.80	3.83
Caltec [9]	total differential	one channel	5.69	3.68
this work	total differential	one channel	6.50	3.60
this work	total differential integral	coupled channel one channel	5.50	3.78

sary. These findings are in contrast to the results found for Ar–CH₄ [7] for which the coupled channel calculation led to a change of parameters in the order of only 1%. However, in this case, the cross sections are dominated by rainbow scattering which is a more classical phenomenon and less affected by the anisotropy than the interference oscillations. This observation is in agreement with the results found for the related glory effect in the velocity dependence of the integral cross section which is also not affected by the molecular character of methane [10]. In the latter experiment, in addition, a quasi-effusive CH₄ beam is used, which leads to a Boltzmann distribution of initial rotational states and thus to an additional averaging of the molecular rotations in contrast to the supersonic nozzle beams used in the experiments for measuring the differential cross sections in which only

the lowest rotational states are populated [6]. The comparison of calculations based on the potential surface of ref. [6] with the glory structure of the integral cross section reveals that the absolute value and thus the long-range part is correctly reproduced but the position of the first glory maximum is shifted to smaller values indicating a too small product of ϵR_m .

Therefore, we have tried to determine a new isotropic potential surface of Ne+CH₄ by fitting it simultaneously to the total differential and the integral cross sections. In this way, we get reliable answers for R_m (diffraction), the product ϵR_m (glories) and the long-range attractive part (absolute values). As potential model a Morse–spline–van der Waals form is used with

$$V_0(R) = f(x)\epsilon, \quad x = R/R_m,$$

Table 2
 Potential parameters for the methane–rare gas systems

	Ne–CH ₄	Ar–CH ₄	Kr–CH ₄	Xe–CH ₄
ϵ (meV)	5.50 ^{a)}	14.04 ^{a)}	17.04 ^{a)}	19.60 ^{a)}
R_m (Å)	3.78 ^{a)}	3.88 ^{a)}	4.02 ^{a)}	4.24 ^{a)}
β	6.97	7.00	7.00	7.00
C_6 (eV Å ⁶)	18.727 ^{b)}	59.363 ^{b)}	93.633 ^{b)}	156.991 ^{b)}
C_8 (eV Å ⁸)	93.633 ^{b)}	296.816 ^{b)}	468.165 ^{b)}	784.956 ^{b)}
x_3	1.10	1.10	1.10	1.10
x_4	1.50	1.50	1.46	1.46
b_1	–0.7481	–0.7466	–0.7466	–0.7466
b_2	1.5741	1.5544	1.6462	1.6269
b_3	–4.7770	–4.8636	–5.1489	–5.2027
b_4	5.1976	5.6980	6.6872	7.1973

^{a)} The estimated uncertainties of the ϵR_m product are about 4% for Ne–CH₄, Kr–CH₄ and Xe–CH₄, whereas it is about 2% for Ar–CH₄, for which the rainbow structure is available. The uncertainty of the R_m value for Ne–CH₄ is about 2% due to the presence of diffraction oscillations.

^{b)} The overall uncertainty in the long-range part of the potential is about 8% due to the uncertainty in the absolute cross section measurements.

$$\begin{aligned}
 f(x) &= \exp[-2\beta(x-1)] \\
 &\quad - 2\exp[-\beta(x-1)], \quad x \leq x_3, \\
 f(x) &= b_1 + (x-x_3) \\
 &\quad \times \{b_2 + (x-x_4)[b_3 + (x-x_3)b_4]\}, \quad x_3 < x < x_4, \\
 f(x) &= -c_6x^{-6} - c_8x^{-8}, \quad x_4 \leq x,
 \end{aligned}$$

with $c_6 = C_6/\epsilon R_m^6$ and $c_8 = C_8/\epsilon R_m^8$.

For the differential cross section CS calculations are performed using the anisotropic potentials V_3 and V_4 from ref. [6]. As was shown in detail in ref. [6] only calculations for the A symmetry are necessary. The individual cross sections are summed and averaged over the overall resolution of the apparatus characterized by $\delta = 1.02^\circ$, the width of the distribution of center-of-mass angles, and $\Delta g/g = 0.08$, the full width at half maximum of the relative velocities [11]. Finally, the calculated cross sections are transformed into the laboratory system for the comparison with the data. The calculations of the integral cross sections are carried out with the spherically averaged potential V_0 using the procedure described in ref. [10]. The resulting potential parameters are given in table 2. The comparison with the data is displayed in fig. 1b for the total differential cross section and in fig. 2 for the absolute integral cross section. The agreement in both cases is quite good. The positions as well as amplitudes of the diffraction oscillations are well reproduced giving a much better fit to the data than obtained previously (see fig. 1a). The fit to the integral cross sections is nearly perfect. The re-

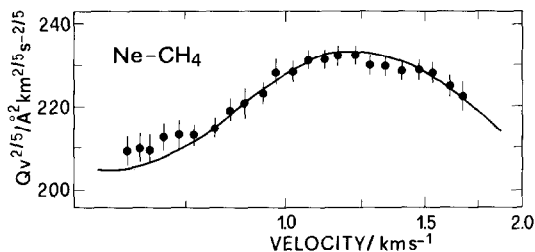


Fig. 2. Absolute integral cross sections Q for Ne-CH₄ as a function of the beam velocity v . The data are plotted as $Qv^{2/5}$ to emphasize the glory structure. The line is the fit obtained using the MSV potential model reported in the text. The bars represent the experimental standard deviation which is about $\pm 1\%$. At low velocities a higher overall uncertainty may be expected mostly due to the thermal averaging.

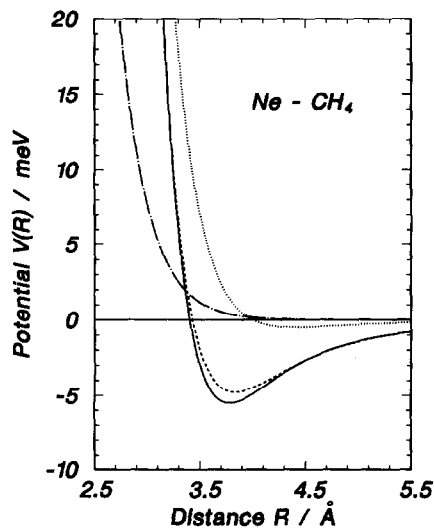


Fig. 3. Comparison of the spherically averaged potentials V_0 for Ne-CH₄ reported in the text (solid line) and in ref. [6] (dashed line). For convenience also the anisotropic part of the potential of ref. [6] is displayed: V_3 (dotted line) and V_4 (dashed-dotted line).

sulting potential is shown in fig. 3. The isotropic part V_0 (solid line) is only different from the potential of ref. [6] in the region of the minimum. R_m is nearly the same (1.3% smaller), while the well depth ϵ is, as expected, 15% larger. The agreement in the short-range part makes a new determination of the anisotropic part of the potential unnecessary, since only this part is relevant for describing the measured inelastic cross sections. Thus we can take V_3 and V_4 which are also shown in fig. 3 for granted. The results for V_0 clearly show that the simple HFD model fails in describing the minimum of the potential correctly. Some attraction in the order of 15% of the well depth has to be added.

3. The methane-heavier rare gas systems

As mentioned above, for Ar-CH₄ a reliable potential surface has been obtained by analyzing the elastic rainbow scattering [7] and the energy loss spectra [8]. The information input brought in by the absolute integral cross section measurement in the glory region [10] allows one to decrease the uncertainty in the potential determination. The glory structure and

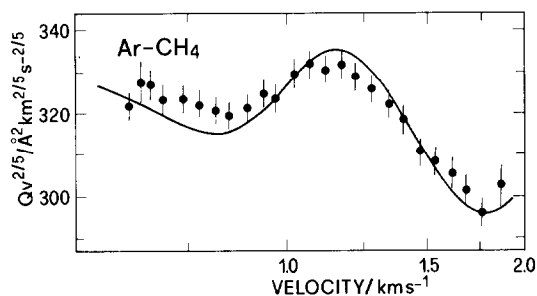


Fig. 4. Absolute integral cross sections Q for Ar-CH₄ as a function of the beam velocity v . The data are plotted as $Qv^{2/5}$ to emphasize the glory structure. The line is the fit obtained using the MSV potential model reported in the text. For the error bars see fig. 2.

the absolute value of the integral cross section can be well reproduced by changing some parameters of the isotropic part of the MSV potential of ref. [7] by only a small amount. This new potential gives also a good fit to the rainbow structure so that it should be preferred for the description of the isotropic Ar-CH₄ interaction. The potential parameters so obtained are reported in table 2. The calculated cross sections based on this potential are compared with the measurements in fig. 4 for the integral cross sections and in fig. 5 for the differential cross sections.

Considering the very similar reduced form observed for Ne-CH₄ and Ar-CH₄ in the well region, a proper determination of meaningful isotropic interaction potentials for Kr-CH₄ and Xe-CH₄ can be ob-

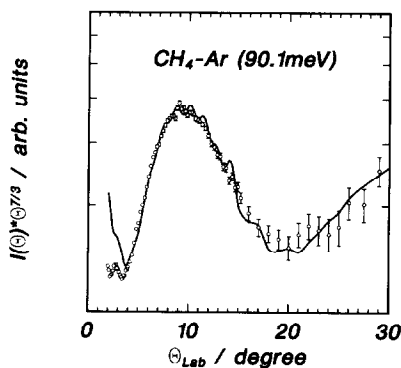


Fig. 5. Measured total differential cross sections for Ar-CH₄ multiplied by $\theta^{7/3}$ in the laboratory system. The peak is the rainbow. The solid line is a CS calculation based on the isotropic MSV potential reported in this work and the anisotropic part of ref. [8].

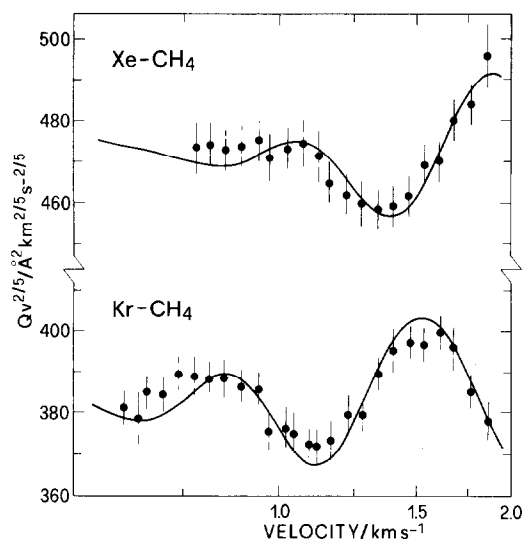


Fig. 6. Absolute integral cross sections Q for Kr-CH₄ and Xe-CH₄ as a function of the beam velocity v . The data are plotted as $Qv^{2/5}$ to emphasize the glory structure. The line is the fit obtained using the MSV potential model reported in the text. For the error bars see fig. 2.

tained by analyzing the integral cross sections previously measured assuming the same reduced form also for these systems. This assumption has been shown to be correct in all those cases where the interaction is of the same van der Waals nature along a homogeneous series [12–14]. In the present case this means taking the same potential MSV model with the same β , χ_3 and C_8/C_6 values. During the analysis the ϵ , R_m and C_6 values are varied to obtain a good fit of both the absolute values of the cross section and the glory extrema positions. The χ_4 parameter is adjusted to obtain the proper connection between the potential at long range and in the well region. The cross sections calculated using the above potentials are shown in fig. 6 compared with the experimental results for Kr-CH₄ and Xe-CH₄, while the potential parameters are reported in table 2.

4. Conclusions

(1) In case that high-pressure supersonic methane beams, which relax to their ground states, are used in a scattering experiment, the diffraction oscillations of the total differential cross section cannot be eval-

uated by a one-channel (elastic) calculation. The complete anisotropic potential surface has to be taken into account. Otherwise an isotropic potential results in a too deep well depth and a too small minimum distance. This conclusion is not true for the glory structure of the integral cross section, in particular if effusive methane beams are used for which the rotational structure is averaged out.

(2) By using total differential cross sections and absolute integral cross sections as input information, a new improved spherically averaged potential surface for Ne-CH₄ is determined with $\epsilon = 5.50$ meV and $R_m = 3.78$ Å.

(3) A similar procedure was used to improve slightly the Ar-CH₄ potential.

(4) By assuming the same reduced form of the isotropic part of the potential for Kr-CH₄ and Xe-CH₄ as that of Ne-CH₄ and Ar-CH₄, realistic potential parameters are obtained for the Kr-CH₄ and Xe-CH₄ systems.

(5) It is noted that all these potentials are essentially probed in the attractive part from the point at which the potential is zero (diffraction oscillations) over the minimum (glory scattering) and the inflection point (rainbow scattering) to the outer attractive wall (absolute integral cross sections).

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