J. Phys. B: At. Mol. Opt. Phys. **33** (2000) 3575–3582. Printed in the UK PII: S0953-4075(00)50160-6

# Low-temperature electron attachment to $CH_3I$

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Received 24 January 2000, in final form 18 April 2000

**Abstract.** Absolute rate coefficients for electron attachment to methyl iodide have been measured under thermal equilibrium conditions between 48 and 300 K. The temperature dependence of our results at low temperatures is found to differ from recent results taken using the laser photoionization attachment (LPA) method. Tentative explanations including possible effects due to electron attachment to clusters are suggested.

## 1. Introduction

Electron attachment to halomethane molecules has been studied by many investigators due to the importance of these compounds in practical applications where the formation of negative ions plays or may play a role and to the fact that many of these compounds exhibit large attachment rate coefficients. Typically, the attachment process is dissociative in nature for these compounds, leading to the production of a negative halogen ion and a neutral carbon-based radical. Thus in the present study, we have examined the dissociative attachment of electrons to methyl iodide, $CH_3I$ and the reaction can be written as

$$e^- + CH_3I \rightarrow CH_3 + I^-. \tag{1}$$

Several authors have published studies in which the temperature dependence of attachment processes has been examined. These studies take several forms. In one type of experiment the temperature of the attaching gas stays constant while the electron energy is changed. In other studies, the attachment is studied under equilibrium conditions where the electron and gas temperatures are equal. In a third type of experiment, the electron and gas temperatures can be varied independently. Until recently, all such studies were limited to measurements with gas temperatures exceeding 200 K although development of the Rydberg atom (RA) [2, 3], threshold photoelectron attachment (TPE) [4, 5] and laser photoelectron attachment (LPA) [6, 7] methods have allowed studies to be made where very low kinetic energy electrons interact with room-temperature gases.

In a recent experiment, [8] the CRESU (cinetique des reactions en ecoulement supersonique uniforme) method has been applied to the study of electron attachment to the halomethanes $CF_3Br$ and $CCl_2F_2$ and to $SF_6$ at temperatures down to 48 K under equilibrium conditions. These experiments yielded results which demonstrated the importance of the internal vibrational energy of the target molecule in determining the efficiency of the electron attachment process and, due to this fact, it was found that for the halomethanes, the CRESU results were strikingly different from those obtained with the RA [9], TPE [4] and drift tube (DT) [10, 11] methods. (For $SF_6$, the effect of internal energy is less acute and the results

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obtained in the CRESU experiment were very similar to those obtained using these other methods.)

The LPA technique has been extended [12] by using a free jet expansion to produce cooling of the target gas. With this improvement, electron attachment to $CH_3I$ has been presented recently [1] together with a theoretical calculation of the reaction cross section. Other published studies of electron attachment to $CH_3I$ have used a variety of different techniques including flowing afterglows (FA) [13, 14], pulse radiolysis [15, 16], electron swarm (ES) [10], electron beam (EB) [17], threshold photoelectron (TPE) [4] and Rydberg atom collisions [2].

In order to examine the effects of internal energy on the rate coefficient, CRESU studies of this attachment reaction have been performed at temperatures between 48 and 300 K and the results thus obtained are presented and discussed below.

## 2. Experimental technique

### *2.1. Apparatus*

The CRESU technique has been described in detail in a number of papers [8, 18, 19], and only its principal features are given here. The reaction chamber is shown in figure 1. An essential element of the apparatus is the Laval nozzle through which a carrier gas (helium, nitrogen or argon) flows continuously, leading to the formation of a supersonic jet whose core is uniform and isentropic. The expansion produces a dramatic cooling of the buffer gas. It is possible to mix other parent or reactant gases in with the carrier gas prior to expansion through the nozzle so that reactions can be studied at very low temperatures. Gas flows of parent, reactant or carrier gas are determined very precisely using Tylan mass flow controllers. In the present case, $CH_3I$ was premixed with helium which was then subsequently injected at different flow rates into the buffer gas in the reservoir upstream of the nozzle.

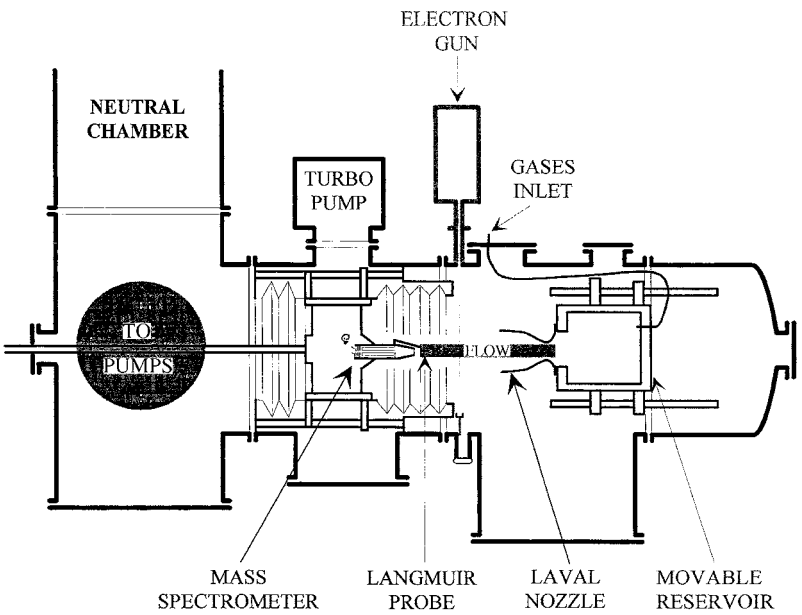


**Figure 1.** Schematic of the CRESU apparatus.

At the exit of the nozzle, the jet is crossed at 90° by a 0.01 mA beam of electrons at an energy of 12 keV and this results in the formation of a weakly ionized plasma with an initial electron density of $10^8$–$10^9$ $cm^{-3}$. Further downstream, a mobile, quadrupole mass spectrometer allows the ions, present in the core of the flow, to be sampled. Ions selected with a given $m/e$ ratio are then detected using a channel electron multiplier, coupled to a counting chain and data acquisition computer. A Langmuir probe, attached to the movable outer casing of the mass spectrometer, can be used to measure the electron density in the flow.

### *2.2. Measurement of the attachment rate coefficient*

Measurements of the rate coefficients for electron attachment are performed using the standard techniques for flow reactors. The equation that governs the development of the electron density $n_e$ in the presence of an attaching gas R (R = $CH_3I$) can be written as

$$v\frac{dn_e}{dx} = D_{ae}\nabla^2 n_e - \alpha[n_+] - \beta[R] \tag{2}$$

where [R] is the density of the gas R, $\alpha$ the coefficient for electron–ion recombination, $\beta$ the electron attachment coefficient, $n_+$, the positive ion density, $v$ the flow speed and $x$ the distance along the flow axis. $D_{ae}$ is the ambipolar diffusion coefficient. As discussed in [8], effects due to diffusion and electron–ion recombination can, in fact, be neglected in this measurement.

Since $[R] \gg [n_e]$, the value of [R] does not change along the flow and so one works in pseudo-first-order conditions. The value of the velocity is constant due to the uniformity of the flow and therefore integration is straightforward, yielding

$$n_e([R]) = n_e([R]_0)\exp\left(-\frac{\beta[R]x}{v}\right). \tag{3}$$

For a given $x$, therefore, the logarithm of the decrease of the electron density with R is a straight line whose slope $p$ is given by $-\beta x/v$. Thus, for two positions of the Langmuir probe along the flow, we obtain two distinct decreases and the difference in the slopes $\Delta p$ gives the attachment coefficient $\beta$, directly from

$$\beta = \frac{v\Delta p}{\Delta x}. \tag{4}$$

The procedure of using the difference in the slopes eliminates any potential experimental effects related to the possible shock wave produced by the presence of the probe in the flow or by the effects of hot electrons in the vicinity of the electron beam. In fact, however, since the Langmuir probe has a diameter less than or equal to the mean free path, one can expect that any perturbation of the supersonic character of the flow will be very small.

## 3. Results and discussion

Rate coefficients measured using the CRESU technique for electron attachment to $CH_3I$ for temperatures between 48 and 300 K are shown in figure 2. Also shown are data taken by Alge *et al* [13] and Burns *et al* [14] using the flowing afterglow technique and by Shimamori and co-workers [15, 16] using a pulse radiolysis method. While our 300 K point is rather high in comparison with other absolute measurements, it is within the error bars, as is the 450 K point of Alge *et al*. It should be noted that this particular measurement was repeated by us several times, using the CRESU apparatus in combination with a subsonic nozzle that had been calibrated on the rate coefficient for electron attachment to $SF_6$ at 300 K. It is interesting

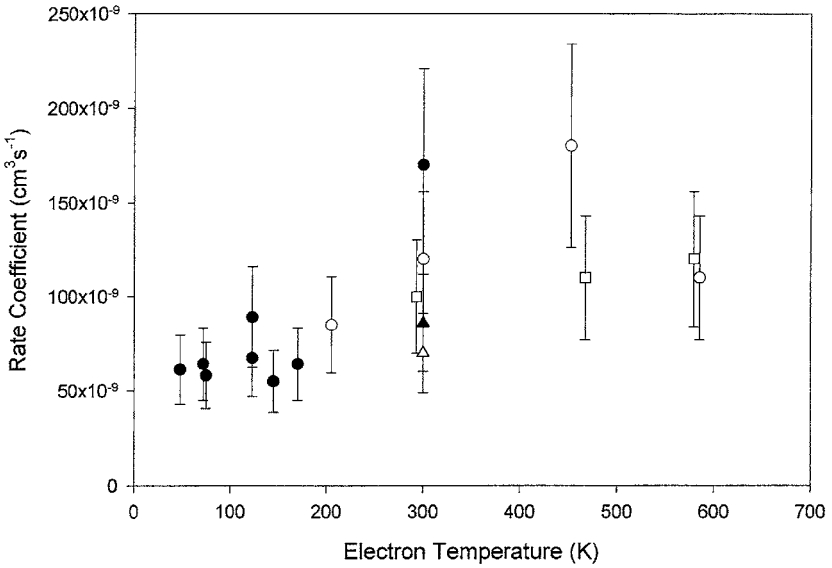


**Figure 2.** Rate coefficients for dissociative attachment to $CH_3I$ versus electron temperature. $T_e = T_g$ for: ●, CRESU; ○, the FALP measurements of [13]; □, [14]; ▲, the pulse radiolysis data of [16]; and △, the drift tube data of [11].

to note that all the results presented in figure 2 are in rather good agreement and display a moderate rise of a factor of two to three over the temperature range shown here. A similar trend was found by Spence and Schulz [17] who used a technique which involved measuring the negative ions formed during the passage of an energy-selected electron beam through a gas target whose temperature was varied. They found an energy-integrated cross section that varied by approximately a factor of 1.5 upon going from a temperature of 300 up to 850 K.

As mentioned in the introduction, other techniques have been used to study electron attachment to $CH_3I$ under non-thermal conditions and the results obtained with these methods are displayed in figure 3 together with the present measurements. The chain curve indicates the data obtained by Alajajian *et al* [4] who employed a threshold photoelectron (TPE) method in which low-energy electrons created by the photo-ionization of krypton gas are observed to attach to methyl iodide vapour which is maintained at a temperature of 300 K. The TPE method is non-absolute and Alajajian *et al*'s results have been renormalized by us to the data of Shimamori and co-workers [15, 16] so that they can be directly compared with the LPA results. Again it is seen that there is a moderate increase in the rate over the range displayed here though in fact, as found in other studies, the rate displays a rapid fall-off above an electron energy equivalent to an electron temperature of about 600 K.

Also shown in figure 3 are the experimental results of [1] taken using the laser photoelectron attachment (LPA) method, with a room-temperature static gas target or using a free jet cooled gas target. These, in turn, are compared with an *R*-matrix theoretical calculation [1]. It is seen that there is excellent agreement between the LPA results and the theory and that these results display a trend similar to that found by the Rydberg atom experiment [2]. This trend is for an increase in the rate coefficient towards lower electron energies and for the results that apply to the case where the gas temperature was held at 300 K, they do not agree with the low-energy data of Alajajian *et al*, which were taken using a room-temperature gas target. It

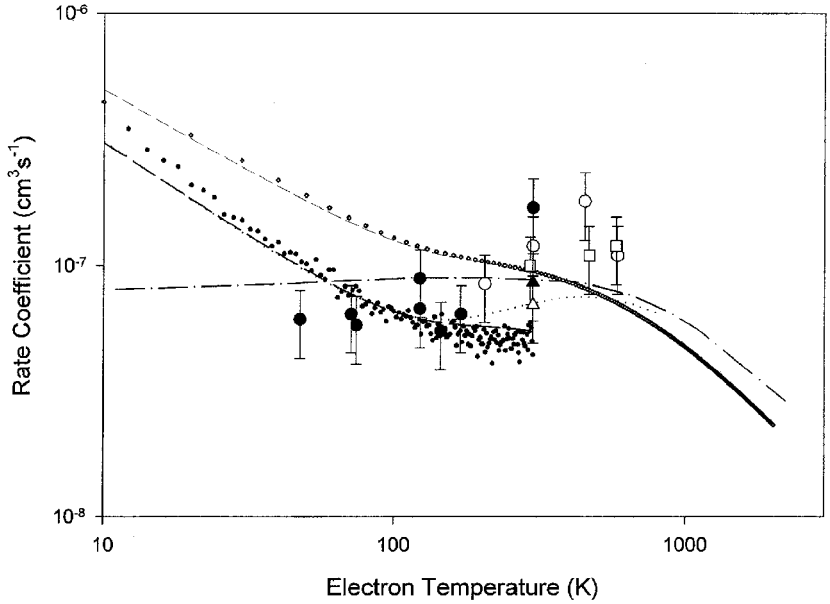


**Figure 3.** CRESU data (●) for attachment to $CH_3I$ presented along with data taken with the following methods: threshold photoelectron (chain curve, $T_g = 300$ K) [4], LPA (◇, $T_g = 300$ K). (•, $T_g = 0$ K) [1]. Theoretical curves for: – – –, $T_g = 300$ K; — — —, for $T_g = 0$ K [1]; and · · · · · ·, for $T_g = T_e$ [22]. Also shown are the experimental data of ○, [13]; □, [14]; ▲, [16]; and △, [11]. The TPE and LPA results were taken at fixed gas temperatures while the electron energy is varied. The CRESU and other experimental results shown were taken under the conditions of $T_g = T_e$.

should be said that the LPA results agree quite well with the TPE results above about 10 meV (see figure 4 of [1]). Schramm *et al* explained the low-energy disagreement as being indicative of the poorer energy resolution of the TPE experiment (see figure 3 of [4]). There is a clear difference between the LPA data and our results though this might perhaps be explained by the fact that in our method, being thermal in nature, the gas temperature is also decreased as the electron temperature decreases. As seen in figure 4, which was calculated using vibrational frequencies for $CH_3I$ taken from the NIST databook [20], at the lower temperatures studied in our work, only the ground vibrational state of the target is significantly populated, while in the other 300 K experimental results, shown here, several vibrational states are populated. If one examines the potential energy curves shown in [1, 21], describing the $CH_3I$ and $CH_3 + I^-$ systems, it is seen that the intersection of these two curves occurs away from the ground vibrational state and therefore one can expect that the attachment rate coefficient will depend very sensitively upon the level of internal excitation of the target. Such an effect has already been demonstrated by us for the cases of attachment to $CF_3Br$ and $CCl_2F_2$ where increasing the gas temperature from 80 to 300 K led to an increase in the attachment rate of over two orders of magnitude.

The LPA results [1], shown in figure 3 for $T_g = 300$ K (gas target) and for $T_g = 0$ K (free jet target) are difficult to reconcile with the CRESU measurements. It should be noted, however, that though the $T_g = 300$ K LPA results are normalized to the data of Shimamori *et al* [15, 16], the $T_g = 0$ K results have been normalized to the 300 K results on the basis of theoretical calculations of the attachment cross section (see [1] for details). A lowering of this

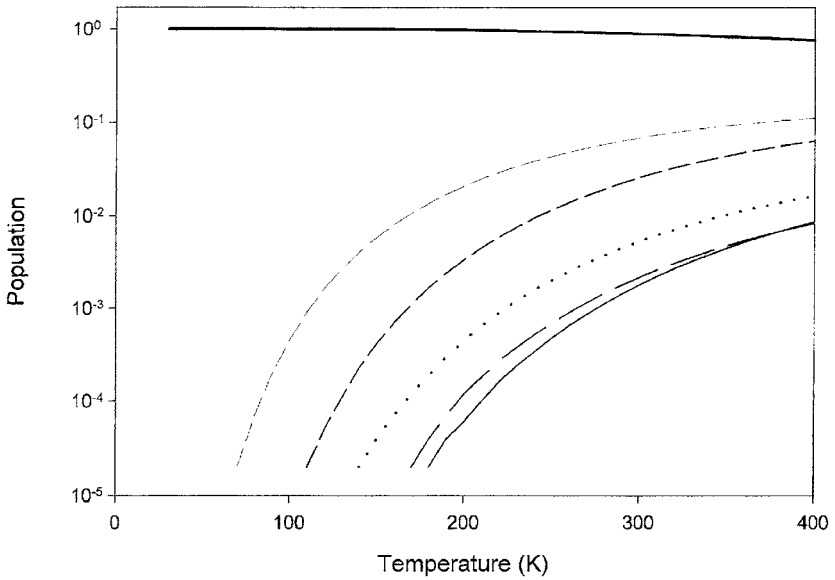


**Figure 4.** Population of vibrational levels of $CH_3I$ versus gas temperature for the following states: ——, (000000); – – –, (0010000); **– – –**, (000001); · · · · · ·, (002000); — — —, (010000); ——, (000010).

normalization would produce a better agreement, though our data do not indicate any evidence for a rise in the attachment rate at low temperature.

The potential energy curves used for the calculations of the theoretical results, presented in figure 3, were constructed from Morse potentials positioned in such a fashion as to reproduce both measured values for the vertical detachment energy of $CH_3I$ and the tendency of the experimental results. In order to do this, the intersection point was located quite close to the ground vibrational level. Other, *ab initio* calculations of the potential energy curves for this system have been calculated by Bertran *et al* [21] and these authors found the intersection to be located considerably further up the neutral molecule curve, i.e. further from the ground vibrational state. Though Bertran *et al* did not perform dynamical calculations of the attachment process, it would be reasonable to assume that their results would generate a much stronger influence of the initial excited state than the results displayed in [1]. Having said this, their results have been criticized in [1] as they yield values for electron affinities that are not in very good accord with experimental values. If the location of the curve crossing between the neutral $CH_3I$ state and the $CH_3 + I^-$ state is such that there will be a strong enhancement of the attachment rate for vibrationally excited molecules, then the apparent disagreement between the LPA results and ours might perhaps be understood in those terms. Fabrikant [22] however, discounts this explanation as moving the crossing away from the ground vibrational state would result in a calculated rate which is much smaller than that measured experimentally.

Our results are taken using various different Laval nozzles which have all been well characterized so that the flow temperatures and velocities are known accurately [8]. The physical parameters of the nozzles used in this study are listed in table 1. In a previous publication [8] we have analysed the efficiency of vibrational relaxation of large molecules in our apparatus and given the number of collisions it seems probable that the molecules will be relaxed to their lowest level at the temperatures encountered in our measurement. We have no definitive proof, however, of the vibrational relaxation of the $CH_3I$ in our experiment as there

**Table 1.** Physical parameters for the nozzles used in the measurement.

| Buffer gas | Temperature (K) | Buffer gas density ($10^{16}$ cm$^{-3}$) | $CH_3I$ density ($10^{11}$ cm$^{-3}$) |
|---|---|---|---|
| $N_2$ | 47.7 | 2.74 | 1.7 |
| $N_2$ | 71.5 | 5.79 | 4.4 |
| $N_2$ | 74.5 | 1.67 | 1.14 |
| He | 123.0 | 12.7 | 7.0 |
| $N_2$ | 145.4 | 9.23 | 5.11 |
| $N_2$ | 169.7 | 0.57 | 0.57 |
| $N_2$ | 300 | 2.45 | 3.1 |

are no reliable data for this process available in the literature but the internal consistency of our results for various nozzle conditions is the best argument in favour of efficient relaxation having occurred. Under free jet conditions (such as in the LPA experiment) it is more difficult to obtain complete vibrational cooling and there is a stronger possibility of residual vibrational excitation of the gas target.

The presence of dimers and higher clusters in the various experiments could also yield strong differences in the rate coefficients for different experimental conditions. For the very low flow rate of $CH_3I$ used in the CRESU measurements such species are unlikely but are present under free jet expansion conditions having a large amount of $CH_3I$ in the flow [23]. Dissociative attachment to van der Waals dimers:

$$(CH_3I)_2 + e^- \rightarrow I^- + CH_3 + CH_3I$$

could be a very efficient process and would be difficult to discriminate from attachment to the monomer since both would yield $I^-$ and detection of this ion is the means of measuring the cross section in the LPA method.

A final possible difference between the LPA and CRESU measurements concerns electron thermalization in the CRESU measurements. In principle, the shape of the $I$–$V$ characteristic generated by a Langmuir probe can be used to measure electron temperature but this method is very inaccurate for low temperatures and therefore we need to rely on estimations of the relaxation time and of possible heating effects. The relaxation time in nitrogen is very short, especially at low energy, and has been discussed in [8]. An experiment recently performed in our laboratory using HCl and HBr as target gases has shown that the electrons are cooled to, at least, well below 500 K in the CRESU flow [24]. This is significant since the attachment rate coefficient decreases for electron temperatures above 500 K. If we had hot electrons in our experiment, that might explain the fact that we do not see a rise in the rate at low gas temperatures but the HBr and HCl measurements rule out this possibility. We have also recently devised an experiment which demonstrated, by means of a measurement of the electron drift velocity, that heating effects, due to possible residual electric fields, are negligible in our experiments [25]. We are confident therefore that the temperatures shown on the abscissa of our figure 3, as they apply to our results, correspond equally to the gas temperature as to the electron temperature and that the explanation of the difference between the various experiments relies on the state of the neutral gas target.

## Acknowledgments

The authors would like to thank H Hotop, M Ruf, I Fabrikant and A Chutjian for useful discussions and for supplying us with their data in tabular form. We should also acknowledge discussions with J-M Saveant concerning the potential curves for $CH_3I$. TS would like to

thank the TMR programme of the European Union for the provision of a postdoctoral research fellowship.

## Appendix

It is interesting to note that Alajajian *et al* had originally compared their TPE data to the flowing afterglow Langmuir probe (FALP) data of Alge *et al* (figure 5 of [4]) for measurements of both $CH_3I$ and $CF_3Br$ and had perhaps implied that the latter data were erroneous since in both cases they appear to intersect the TPE data almost orthogonally. As seen in figure 2, however, the FALP data, in fact, simply display a scatter which is within the error bars and the overall trend of the rate coefficient is almost flat in this temperature region. In contrast, complementary measurements of attachment to $CF_3Br$ made using the CRESU technique [8] show that, in this case, there is a steep rise in the rate coefficient with temperature and that a downward extrapolation of the FALP results to lower temperature is closely followed by the CRESU results.

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