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Electron-impact rotational excitation of the carbon monosulphide (CS) molecule

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ABSTRACT

Rotational excitation of the carbon monosulphide (CS) molecule by thermal electron-impact is studied using the molecular **R**-matrix method combined with the adiabatic-nuclei-rotation (ANR) approximation. Rate coefficients are obtained for electron temperatures in the range 5–5000 K and for transitions involving levels up to $J = 40$. It is confirmed that dipole allowed transitions ($\Delta J = 1$) are dominant and that the corresponding rate coefficients exceed those for excitation by neutrals by at least five orders of magnitude. As a result, the present rates should be included in any detailed population model of CS in sources where the electron fraction is larger than $\sim 10^{-5}$, in particular in diffuse molecular clouds and interstellar shocks.

Key words: molecular data – molecular processes – scattering.

1 INTRODUCTION

Carbon monosulphide (CS) was discovered in the interstellar medium by Penzias et al. (1971) through the $J = 3 \rightarrow 2$ millimeter emission line. Since then, the CS molecule has been extensively observed in a variety of regions, from dense and diffuse molecular clouds (e.g. Snell, Langer & Frerking 1982; Lucas & Liszt 2002) to interstellar shocks (e.g. Thronson & Lada 1984) and comets (e.g. Boissier et al. 2007). In addition to millimeter emission and absorption lines, interstellar CS has been recently identified *via* ultraviolet absorption (Destree, Snow & Black 2009). Along with other sulphur-bearing molecules, CS is an interesting species because gas-phase chemistry models fail to reproduce its abundance by large factors, both in dark and diffuse gas (Lucas & Liszt 2002, and references therein). As explained by these authors, the CS abundance is consistent with the observed amounts of HCS^+ (if CS is formed via dissociative recombination), but the abundances of the expected precurors of the ion are 1–2 orders of magnitude too low in diffuse clouds, where the electron fraction is large.

In order to accurately derive the CS abundance from the observations, a good knowledge of collisional rate coefficients is necessary. In dark clouds, the dominant colliding partners are H_2 molecules. Scattering calculations on the rotational excitation of CS by $H_2(J = 0)$ were first performed by Green & Chapman (1978). Turner et al. (1992) subsequently extended these to higher rotational levels (up to $J = 20$) and temperatures (up to 300 K). More recently, Lique, Spielfiedel & Cernicharo (2006) have performed extensive scattering calculations for the CS–He system based on a high-accuracy potential energy surface (PES). These authors have suggested that their CS–He rate coefficients (scaled by a factor of 1.4 to account for the ratio of the reduced mass between CS–H_2 and CS–He) could presently be the most appropriate for interpreting CS observations in dense clouds, owing to the limited accuracy of the CS–H_2 PES used by Green & Chapman (1978) and Turner et al. (1992). On the other hand, the scaled He rates were found to agree with the $H_2(J = 0)$ rates to within a factor of about 2.

In diffuse regions with high fractional ionization such as diffuse or translucent clouds and shocks, H atoms and free electrons are expected to play an important role in the excitation of molecular species. To our knowledge, there are no data for the CS–H system and no explicit calculations are available for the electron-impact excitation of CS. However, rate coefficients for the CS–electron system have been estimated by some authors (e.g. Drdla, Knapp & van Dishoeck 1989; Turner 1996) using the analytical formula (equation 1) of Dickinson et al. (1977). Drdla et al. (1989) have in particular shown that electron-impact rates for dipolar transitions ($\Delta J = 1$) are typically five orders of magnitude greater than the corresponding H_2 rates. This large difference between electron and H_2 (and also H atoms) reflects both the strong electron–dipole interaction and the much lower mass of electrons relative to hydrogen. Drdla et al. (1989) concluded that electron collisions completely dominate the CS excitation in diffuse clouds where the electron fraction is larger than 10^{-5}. We note that this conclusion was also reached for other neutral polar molecules, e.g. SiO (Varambhia et al. 2009).

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In the formalism of Dickinson et al. (1977), as in the Born approximation (Dickinson & Richards 1975), it is assumed that collisional rates can be determined by long-range interactions only. The further standard approximation is to consider only the dominant long-range term, that is the charge–dipole interaction in the case of a polar target. Such a model obviously predicts rates for dipolar transitions only. The recent **R**-matrix studies of Tennyson and collaborators have shown, however, that transitions with $\Delta J > 1$ have significant rates and are completely dominated by short-range interactions (e.g. Faure, Gorfinkiel & Tennyson 2004a, in the case of water). In the case of strongly polar targets such as HCN or SiO, dipolar transitions were still found to largely dominate over other transitions (see Faure et al. 2007; Varambhia et al. 2009, respectively). For the strongly polar water molecule, it has been possible to compare results from this procedure with experiment and it has been demonstrated to give excellent results (Faure, Gorfinkiel & Tennyson 2004b; Zhang, Faure & Tennyson 2009).

In the present study, as in the previous ones, the molecular **R**-matrix method has been combined with the adiabatic-nuclei-rotation (ANR) approximation. Our aim is to provide accurate rate coefficients for the electron-impact rotational excitation of CS within a large temperature range (5–5000 K) and for a large number of rotational levels ($J = 0$–40). In Section 2, **R**-matrix calculations are described and the procedure used to obtain rotational rates is briefly introduced. In Section 3, both cross-sections and rate coefficients are presented and compared to previous data. Conclusions are given in Section 4.

2 CALCULATIONS

The **R**-matrix calculations were based on a recent study of dissociative electron attachment to CS (Graupner et al., in preparation) which was performed using the Quantemol-N (Tennyson et al. 2007) implementation of the UK polyatomic **R**-matrix codes of Morgan, Tennyson & Gillan (1998). Calculations were performed for CS fixed at its equilibrium bondlength of 1.5349 Å (NIST 2008) using C_{2v} symmetry. Target molecular orbitals were obtained from a self-consistent field calculation performed using a double zeta plus polarization (DZP) basis set. 48 target states were generated from a model which froze the carbon $1s$ and sulphur $1s$, $2s$ and $2p$ electrons, and let the remaining 10 electrons move freely among the low-lying molecular orbitals whose symmetry corresponds to the C $2s$ and $2p$, and S $3s$ and $3p$ orbitals. This model gives a permanent dipole for CS of 1.783 D, about 10 per cent less then the measured value of 1.958 ± 0.005 D (Winnewisser & Cook 1968). Further details of the target model can be found in Graupner et al. (in preparation).

The scattering calculations were performed with an **R**-matrix sphere of 12 a_0. The continuum was represented by Gaussian Type Orbitals (GTOs) in a partial wave expansion up to g-waves ($l = 4$) (Faure et al. 2002); in addition, two a_1, one b_1 and one b_2 target virtual orbitals were also retained. In the outer region, **T**-matrices were calculated from 0.02 to 3.88 eV, just below the first electronic excitation threshold (3.90 eV) from **K**-matrices obtained by propagating the (300-channel) **R**-matrix to a radius of 100.1 a_0. The measured value of the dipole moment was used both in the outer region and for the Born correction described below. As a final step, in these calculations the C_{2v} symmetry **T**-matrices were converted into $C_{\infty v}$ symmetry appropriate for the CS molecule. As a check, we also calculated the rotationally resolved integral cross-sections using the cc-pVTZ basis set, for which an **R**-matrix radius of 12 a_0 was again found adequate. Use of this target basis made little difference to our calculated cross-sections, with the exception that the $^2\Pi$ shape resonance moved to higher energy compared to the corresponding DZP calculation.

To convert these body-frame, low-l results into converged rotational excitation cross-sections a standard Born top-up procedure along with a frame transformation was used.

This procedure is based upon the adiabatic nuclear-rotation (ANR) approximation which assumes all rotational levels are degenerate. The known unphysical behaviour of the excitation cross-sections at low energy (near rotational thresholds) was corrected using a simple kinematic ratio, as in Faure et al. (2004a). For dipole-allowed excitation ($\Delta J = 1$) transitions, the total cross-section was calculated as the total dipole Born cross-section plus the calculated **R**-matrix cross-section minus the dipole Born cross-section for $l \leq 4$. The comparison of rates given below shows that this procedure gives slightly reduced rates for $\Delta J = 1$ transitions compared to simply using the Born approximation. Our previous works (Faure & Tennyson 2001; Faure et al. 2007) showed that such a completion procedure, based on the quadrupole or induced dipole Born approximation, gave a negligible contribution to transitions with $\Delta J \geq 2$, so it was not attempted.

The calculated cross-sections were converted to rates using a standard Maxwellian distribution for the electron velocities. Our cross-sections were extended to very low collision energies (below 0.02 eV) using the extrapolation formula of Rabadán, Sarpal & Tennyson (1998), which is consistent with the above threshold correction. We stress that the exact threshold law is not known in the case of neutral targets (see Faure et al. 2007). As a result, the uncertainties in the low temperature rate calculation, due to both this procedure and our complete neglect of closed-channels effects, will mean that our results are less reliable at temperatures below ~100 K; for this region, we estimate an accuracy of only a factor of 2 to 3.

3 RESULTS AND DISCUSSION

Fig. 1 gives electron-impact rotational excitation cross-sections for transitions starting from CS in its rotational ground state. As expected, the cross-section is dominated by the $\Delta J = 1$ transition. Our procedure shows that the pure dipole Born calculation slightly overestimates the contribution to the cross-section of the lowest partial waves. The cross-sections for both the $\Delta J = 2$ and 3 transitions show a pronounced feature at about 0.3 eV. This is the

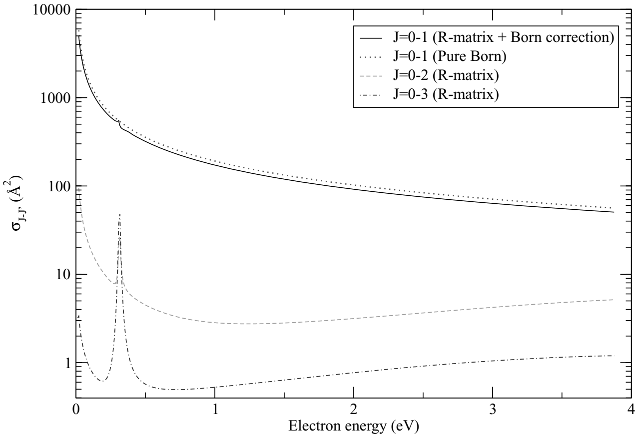

Figure 1. Electron-impact rotational excitation cross-sections for the CS molecule in its rotational ground state.

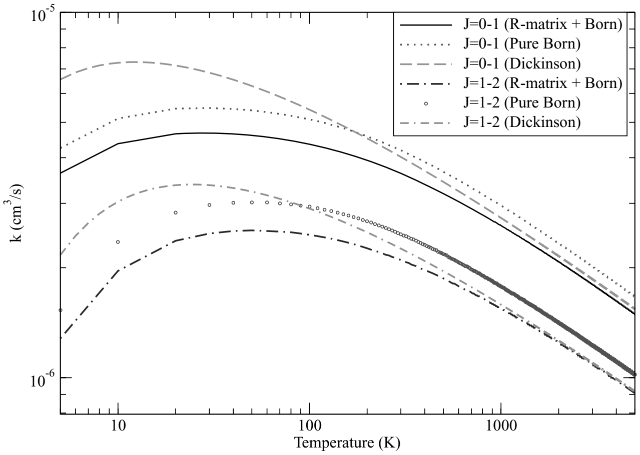

Figure 2. Electron-impact rotational excitation rates for the CS molecule for $\Delta J = 1$ transitions starting from the $J = 0$ and 1 levels. The results of a pure dipole Born calculation and the formula of Dickinson et al. (1977) are given for comparison.

well-known shape resonance which leads to dissociative attachment of CS (Graupner, Field & Feketeova 2006); this and other resonances were analysed in our previous work on electron collisions with CS (Graupner et al., in preparation). Our ANR-based procedure is not reliable for collisions in the region of resonances since the collision time can become longer than the rotational period. However, the enhancements displayed by the cross-section in this region probably represent a reasonable first approximation to the increased cross-section due to the resonance.

Fig. 2 compares our rates with those given by a pure dipole Born calculation and by the analytic formula of Dickinson et al. (1977). Our calculated rates for $\Delta J = 1$ are comparable to, but slightly lower than, these estimates. The comparison is only made for transitions with $\Delta J = 1$ as the approximate procedures assume that these are the only transitions that contribute.

Since for modelling it is most convenient to use analytic forms for rates, we have fitted our de-excitation rates to the standard form of Faure et al. (2004a):

$$\log_{10} k(T) = \sum_{r=0}^{N} a_r x^r, \tag{1}$$

where $x = T^{-1/6}$ and $N = 4$ were used. This formula was applied to rates involving states with $J \leq 40$ and $\Delta J \leq 8$. Fits were performed for the temperature range 5–5000 K, which was split into three subranges 5–190, 190–780 and 780–5000 K, chosen so as to achieve an accuracy of a few per cent (global maximum fitting errors 14, 6 and 4 per cent, respectively). The coefficients for the temperature range 5–190 K are tabulated in Table 1 in units such that the rate constant, $k(T)$, is given in cm^3 s^{-1}. The entire set of fit coefficients can be obtained electronically from the supporting material associated with this article. Excitation rates can be obtained from the principle of detailed balance.

Fig. 3 gives a comparison of rotational excitation rates for CS collisions with electrons, para-H_2 and He. It can be seen that electron-impact excitation is clearly much more efficient at stimulating this process, with a collisional excitation rate about five orders of magnitude larger across the entire temperature range under consideration. We note that collisional excitation by ortho-H_2 may be a few times faster than the corresponding para-H_2 rate, but we do not have ortho-H_2 data to compare with.

Table 1. Electron-impact rotational de-excitation rates fitting coefficients for the temperature range 5–190 K, see equation (1).

J'	J''	E_{up} (K)	a_0	a_1	a_2	a_3	a_4
1	0	2.4	−9.333	21.489	−49.860	52.273	−20.561
2	0	7.1	−10.554	13.608	−24.244	21.891	−8.071
2	1	7.1	−9.163	20.629	−48.177	51.008	−20.346
3	0	14.1	−11.277	7.911	−10.071	5.862	−1.367
3	1	14.1	−10.177	11.622	−18.648	14.677	−4.711
3	2	14.1	−8.962	19.271	−44.892	47.445	−18.910
4	0	23.5	−12.829	5.333	−3.640	−1.787	2.046
4	1	23.5	−11.302	8.988	−12.767	8.395	−2.192
4	2	23.5	−10.232	12.405	−20.755	16.874	−5.558
4	3	23.5	−7.882	11.491	−24.392	23.718	−8.758
5	0	35.3	−13.799	−2.878	15.798	−22.588	10.405
5	1	35.3	−12.463	3.612	1.250	−8.286	5.223
5	2	35.3	−11.404	10.154	−15.819	11.532	−3.335
5	3	35.3	−10.552	14.834	−26.988	23.626	−8.249
5	4	35.3	−9.113	20.258	−47.686	50.759	−20.356
6	0	49.4	−3.350	−85.535	215.001	−234.816	94.624
6	1	49.4	−13.390	−4.605	20.011	−27.510	12.590
6	2	49.4	−13.027	8.331	−11.796	7.141	−1.478
6	3	49.4	−11.209	9.062	−13.073	8.254	−1.874
6	4	49.4	−10.390	13.781	−24.112	19.974	−6.541
6	5	49.4	−8.290	14.364	−32.328	33.171	−12.899
7	0	65.8	6.834	−167.254	410.048	−440.921	175.877
7	1	65.8	−2.259	−91.225	227.909	−248.158	99.861
7	2	65.8	−13.435	−3.647	17.160	−24.220	11.249
7	3	65.8	−13.374	11.194	−19.611	16.172	−5.292
7	4	65.8	−10.828	6.490	−6.233	0.067	1.756
7	5	65.8	−10.563	15.067	−27.355	23.345	−7.808
7	6	65.8	−8.579	16.276	−37.147	38.382	−14.959
8	0	84.6	14.378	−206.625	492.452	−516.735	201.704
8	1	84.6	5.859	−158.026	383.426	−408.613	161.702
8	2	84.6	−2.293	−89.820	222.874	−241.470	96.797
8	3	84.6	−13.379	−3.577	16.588	−23.438	10.921
8	4	84.6	−13.183	10.024	−16.480	12.204	−3.400
8	5	84.6	−10.537	4.415	−0.408	−7.302	5.202
8	6	84.6	−10.319	13.498	−23.480	18.986	−5.976
8	7	84.6	−8.119	13.082	−29.156	29.606	−11.399

Note. E_{up} gives the upper state energy in K. The full version of this table is available with the online version of the article (see Supporting Information). The energies E_{up} are from the Cologne Database for Molecular Spectroscopy catalogue as given in http://www.strw.leidenuniv.nl/~moldata/datafiles/cs.dat.

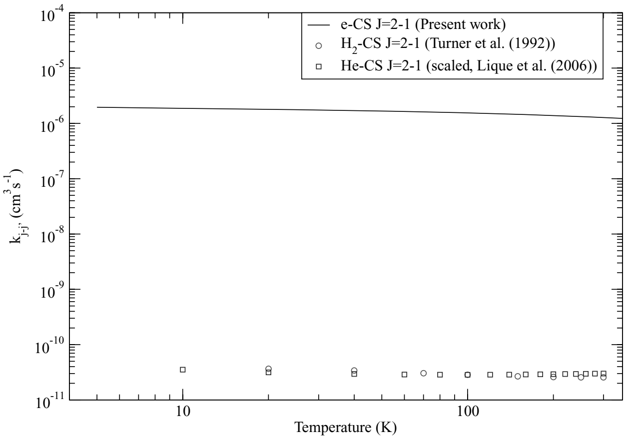

Figure 3. Electron, para-H_2 and He impact rotational de-excitation rates for the CS molecule for $\Delta J = 1$ transitions starting from the $J = 2$ level. The He data were scaled up by a factor of 1.4 as mentioned in the introduction.

4 CONCLUSIONS

We report extensive calculations on rotational excitation of the CS molecule by low-energy electrons. Excitation of transitions with $\Delta J = 1$ is the most likely process, with $\Delta J = 2$ transitions, the next most likely process, being at least an order of magnitude less likely. Comparisons between the $\Delta J = 1$ excitation rates and the corresponding rates for other important interstellar projectiles suggests that the role of electron collisions cannot be neglected in any interstellar environment where the electron fraction is likely to be larger than about 10^{-5} that of hydrogen. Such environments include diffuse molecular clouds and interstellar shocks.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Table 1. Electron-impact rotational de-excitation rates fitting coefficients for the temperature range 5–190 K.

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