

The rotational excitation of CO by H₂

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Abstract

Cross sections and rate coefficients have been calculated for the rotational excitation of CO by ground state ortho- and para-H₂. The quantum-mechanical-coupled-channels method was used, without significant approximations other than the finite size of the basis sets. For collisions with ortho-H₂, rotational levels of CO $j \leq 20$ were included, and $j \leq 29$ for collisions with para-H₂. Comparison is made with recent calculations by Mengel *et al* (2001 *Can. J. Phys.* at press).

1. Introduction

In the context of the interstellar medium, H₂ and CO are both important molecules, H₂ because of its high abundance, and CO because its low-frequency rotational transitions occur at mm wavelengths and are readily excited, even at low-kinetic temperatures, and observable from the ground. Carbon monoxide is the most abundant interstellar molecule (after H₂) and has been extensively observed in order to estimate the mass of molecular gas in our own and in other galaxies. CO is currently the only molecule to have been observed in galaxies at high redshift (see Combes (2000)), providing a link with much earlier stages in the evolution of the Universe and with galaxy formation.

At the low temperatures which characterize interstellar molecular clouds, collisions between H₂ and CO molecules induce rotational transitions in CO, which has a much smaller rotational constant than H₂. Quantum mechanical studies of this process have been undertaken by Green and Thaddeus (1976), who used a scaled He–CO interaction potential, and by Flower and Launay (1985) and Schinke *et al* (1985), who used (different) *ab initio* H₂–CO potential energy surfaces (PES). Very recently, Mengel *et al* (2001) have employed the H₂–CO PES of Jankowski and Szalewicz (1998) to recompute cross sections and rate coefficients for rotational transitions in CO. Only Flower and Launay (1985) and Mengel *et al* (2001) have considered collisions involving H₂ molecules in rotational states $j_1 > 0$, specifically $j_1 = 1$ (ground state ortho-H₂), in addition to $j_1 = 0$ (ground state para-H₂).

In view of the importance of the H₂–CO system in astronomy, we decided to perform more extensive calculations of the rotational excitation of CO by both ortho- and para-H₂. Mengel *et al* (2001) present results for transitions between rotational levels of CO $j_2 \leq 8$ only, whereas observations of CO extend to much larger values of the rotational quantum number (cf Justtanont *et al* (2000)). In this paper, we use a basis of levels of CO $j_2 \leq 29$, in the case

Table 1. Geometries at which the H₂–CO interaction potential was generated; see section 2.1.

θ_1	θ_2	ϕ
0.0	0.0	0.0
90.0	0.0	0.0
0.0	30.0	0.0
90.0	30.0	0.0
90.0	30.0	90.0
0.0	60.0	0.0
90.0	60.0	0.0
90.0	60.0	90.0
0.0	90.0	0.0
90.0	90.0	0.0
90.0	90.0	90.0
0.0	120.0	0.0
90.0	120.0	0.0
90.0	120.0	90.0
0.0	150.0	0.0
90.0	150.0	0.0
90.0	150.0	90.0
0.0	180.0	0.0
90.0	180.0	0.0
45.0	30.0	0.0
45.0	45.0	0.0
45.0	60.0	0.0
45.0	120.0	0.0
45.0	135.0	0.0
45.0	150.0	0.0

of scattering on para-H₂ ($j_1 = 0$), and $j_2 \leq 20$, for scattering on ortho-H₂ ($j_1 = 1$). At low temperatures, resonances in the cross sections for rotationally inelastic scattering prove to be important in determining the thermal rate coefficients.

2. Method

2.1. Interaction potential

Following the conventions of Jankowski and Szalewicz (1998), let \mathbf{R} denote the vector from the centre of mass of the H₂ molecule (1) to the centre of mass of the CO molecule (2). Let \mathbf{r}_1 and \mathbf{r}_2 denote the intramolecular H–H and C–O vectors; that of CO is taken in the sense O \rightarrow C. In the body-fixed coordinate system, in which the z -axis is coincident with the direction of \mathbf{R} , the spherical polar angles which define the orientations of the intramolecular axes are (θ_1, ϕ_1) and (θ_2, ϕ_2) ; $\theta_1 = \mathbf{r}_1 \cdot \mathbf{R}/(r_1 R)$ and $\theta_2 = \mathbf{r}_2 \cdot \mathbf{R}/(r_2 R)$. The interaction potential $V(R, \theta_1, \theta_2, \phi)$, where $\phi = \phi_2 - \phi_1$, was evaluated with r_1 and r_2 fixed at their average values in the respective ground rovibrational states (Jankowski and Szalewicz 1998). Thus, V is a ‘rigid rotor’ potential. The interaction energy was evaluated, using the Fortran programme supplied by Jankowski and Szalewicz, on the grid of 25 distinct geometries which are listed in table 1, for values of the intermolecular distance in the range $4 \leq R \leq 20$ bohr; an exponential cut-off was applied beyond $R = 20$. The potential was then fitted to the functional

Table 2. Angular symmetries retained in the expansion (equation (1)) of the H₂–CO interaction potential.

q_1	q_2	μ
0	0	0
0	1	0
0	2	0
0	3	0
0	4	0
0	5	0
0	6	0
2	0	0
2	1	0
2	2	0
2	3	0
2	4	0
2	5	0
2	6	0
2	1	1
2	2	1
2	3	1
2	4	1
2	5	1
2	6	1
2	2	2
2	3	2
2	4	2
2	5	2
2	6	2

form

$$V(R, \theta_1, \theta_2, \phi) = \sum_{q_1 q_2 \mu \geq 0} \nu_{q_1 q_2 \mu}(R) \frac{4\pi}{[2(1 + \delta_{\mu 0})]^{1/2}} [Y_{q_1 \mu}(\theta_1, \phi_1) Y_{q_2 - \mu}(\theta_2, \phi_2) + Y_{q_1 - \mu}(\theta_1, \phi_1) Y_{q_2 \mu}(\theta_2, \phi_2)] \quad (1)$$

where $Y_{q\mu}$ denotes a normalized spherical harmonic function. The values of the interaction potential at the grid points in table 1 are reproduced exactly by the set of expansion coefficients, $\nu_{q_1 q_2 \mu}(R)$, with the orders given in table 2.

Mengel *et al* (2001) used a modified version of the potential computed by Jankowski and Szalewicz (1998). Studies of the second virial coefficient (Gottfried and McBane 2000) had suggested that the depth of the attractive well of the PES should be reduced by a factor of 0.93. Mengel *et al* (2001) scaled the entire potential by this factor and obtained improved agreement with measurements of pressure broadening cross sections. Accordingly, we performed additional sets of calculations, in which: (a) the isotropic part of the interaction potential, i.e. the coefficient $\nu_{000}(R)$ in equation (1), was multiplied by a factor of 0.93 in the range $6.5 \leq R \leq 10$ bohr, which covers the region of the potential minimum; and (b) the entire interaction potential (1) was scaled by this same factor, for all R . As we report in section 3 below, this scaling had only minor consequences for the computed values of the rate coefficients, and the results presented here were obtained with the unscaled interaction potential.

2.2. Scattering

We have used the Molcol quantum mechanical scattering code (Flower *et al* 2000) to perform the rigid rotor calculations reported below. The full-coupled-channels method was employed, without further approximations, other than the use of finite basis sets. Measured values of the rotational eigenenergies of CO were taken from <http://spec.jpl.nasa.gov/> (Pickett *et al* 1998). For the scattering of CO on para-H₂, the basis comprised rotational states $j_2 \leq 29$ on CO and $j_1 = 0$ on H₂, giving rise to a maximum of 465 coupled channels. For the scattering on ortho-H₂, $j_2 \leq 20$ and $j_1 = 1$ generated up to 672 coupled channels. The corresponding sets of coupled differential equations were integrated using the Johnson–Manolopoulos method (Johnson 1973, Manolopoulos 1986). Cross sections were obtained on a grid of barycentric collision energies in the range $6 \leq E \leq 4000$ K, in steps which increased (with E) from 0.5 to 50 K. At each energy, the number of partial waves was sufficient to ensure the convergence of the inelastic cross sections.

Our calculations were performed in the ‘rigid rotor’ approximation, the CO bond length being fixed at its average value in the ground state. It follows that coupling to excited vibrational states of CO was excluded from the calculations. Rotational states of CO $j_2 \leq 29$ were considered; the level $j_2 = 29$ lies approximately 2400 K above the $j_2 = 0$ ground state. On the other hand, the vibrational energy spacing in CO is 3100 K, and so we are confident that the coupling between the rotational levels included in the bases dominates that (which we neglect) to excited vibrational states.

Mengel *et al* (2001) used a version of the Molscat code of Hutson and Green (1995), as modified by McBane (Antonova *et al* 2000) in order to incorporate the H₂–CO interaction potential generated by the Fortran programme of Jankowski and Szalewicz (1998). Thus, the present calculations are entirely numerically independent of those performed by Mengel *et al*.

Rate coefficients for downwards (de-excitation) transitions were computed from the cross sections, Q , as

$$q(T) = \left(\frac{8kT}{\pi m} \right)^{1/2} \int_0^\infty Q(x) x e^{-x} dx \quad (2)$$

where $x = E/kT$; E is the barycentric collision energy, T is the kinetic temperature and m is the reduced mass of the colliding pair of molecules. The integral was evaluated by means of a trapezoidal rule on a fine grid of $0 \leq x \leq 10$, the integrand at the quadrature points being generated by cubic spline interpolation of the values deriving from the scattering calculations. The rate coefficients for the reverse (excitation) transitions were obtained from the detailed balance relation.

3. Results

Mengel *et al* (2001) presented rate coefficients for rotational transitions in CO, induced by H₂. They compared a subset of their results with the earlier calculations of Green and Thaddeus (1976), Flower and Launay (1985) and Schinke *et al* (1985), for collisions with para-H₂ ($j_1 = 0$) at $T = 10$ and 40 K. For this same subset of transitions, we compare, in table 3, the present calculations with those reported by Mengel *et al*.

The level of agreement between the two independently calculated sets of results may be seen to be good. At $T = 10$ K, the rms deviation is 17%, and 11% at 40 K. The lower the temperature, the more sensitive are the cross sections to the vicinity of the minimum and the long-range part of the interaction potential. This sensitivity is, in the system under study, enhanced by the existence of resonances in the cross sections in the region above the threshold.

Table 3. A comparison of the rate coefficients (in units of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$) for de-excitation transitions between rotational levels j_2 of CO, induced by para-H₂ ($j_1 = 0$).

Initial	Final	This work	Mengel <i>et al</i>
$T = 10 \text{ K}$			
1	0	0.281	0.256
2	0	0.229	0.241
3	0	0.064	0.047
4	0	0.020	0.021
5	0	0.007	0.005
2	1	0.697	0.644
3	1	0.412	0.418
4	1	0.114	0.087
5	1	0.042	0.042
3	2	0.816	0.734
4	2	0.526	0.554
5	2	0.153	0.110
4	3	0.888	0.793
5	3	0.656	0.721
5	4	0.925	0.672
$T = 40 \text{ K}$			
1	0	0.306	0.292
2	0	0.285	0.292
3	0	0.078	0.061
4	0	0.028	0.029
5	0	0.012	0.011
2	1	0.622	0.569
3	1	0.464	0.470
4	1	0.141	0.117
5	1	0.051	0.054
3	2	0.700	0.616
4	2	0.558	0.575
5	2	0.186	0.153
4	3	0.720	0.671
5	3	0.641	0.676
5	4	0.784	0.648

As the threshold is approached, the cross sections ultimately increase, as may be seen from the examples plotted in figure 1; this behaviour was first predicted by Wigner (1948). Beyond their respective thresholds, the cross sections show a resonance structure which makes important contributions to the rate coefficients for these transitions at low temperatures. At least some, perhaps all of the resonances are of the ‘shape’ type, associated with maxima in the ‘effective’ potential, which is the sum of the electrostatic interaction, considered in section 2.1, and the centrifugal (repulsive) potential, arising from the relative motion of the two molecules. We established that the resonances are ‘shape’ rather than ‘Feshbach’ in origin by means of a two-state calculation of the $1 \rightarrow 0$ cross section, in which coupling to other excited states was absent. The resonance structure remained, although it differed in detail from that shown in figure 1. Furthermore, we have considered the partial-wave contributions to one of the resonances and computed the corresponding effective potential; this analysis confirmed the identification of a shape resonance. In view of the structure in the cross sections, apparent in

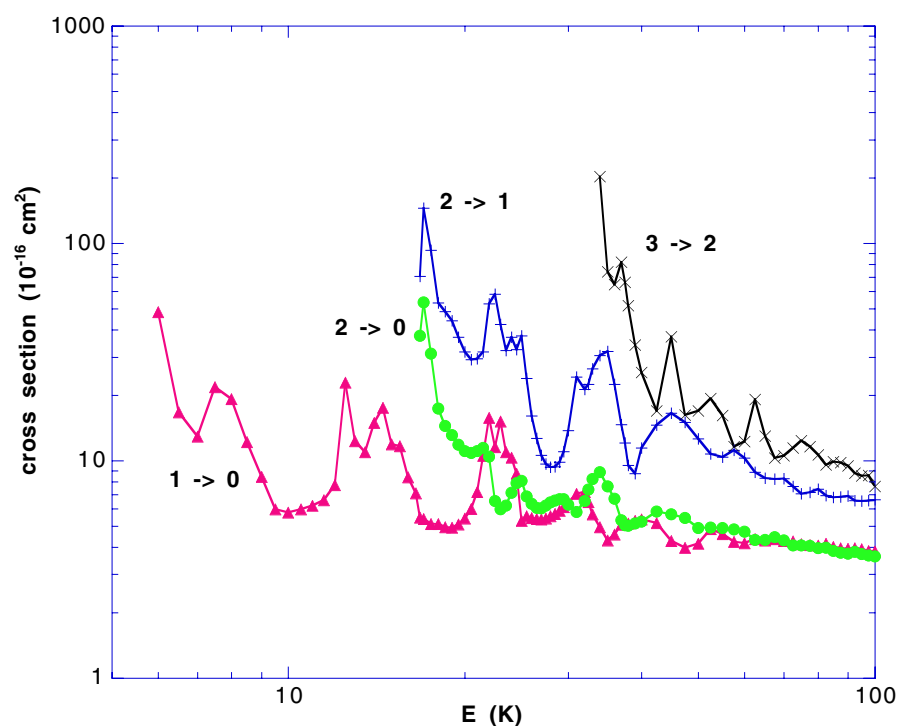


Figure 1. Resonances in the cross sections of a selection of rotational de-excitation transitions in CO, induced by para-H₂ ($j_1 = 0$). Triangles, $j_2 = 1 \rightarrow 0$; circles, $2 \rightarrow 0$; vertical crosses, $2 \rightarrow 1$; diagonal crosses, $3 \rightarrow 2$.

(This figure is in colour only in the electronic version, see www.iop.org)

figure 1, a fine grid of collision energies is deemed necessary as threshold is approached in order to reliably determine the rate coefficients.

Although straightforward in principle, the calculation of the rate coefficients from the cross sections requires care in practice. In addition to sampling adequately the resonance structure near the thresholds, the collision energies must extend sufficiently high to ensure the convergence of the integral in (2), notably as the temperature T increases. In this respect, we note that some of the results of Mengel *et al* (2001) may be inadequately converged. Their collision energy grid extended to $E = 400 \text{ cm}^{-1}$ ($1 \text{ cm}^{-1} = 1.4388 \text{ K}$) for collisions with para-H₂ and $E = 300 \text{ cm}^{-1}$ for collisions with ortho-H₂. Relative to the highest rotational level of CO for which they tabulated the de-excitation rate coefficients ($j_2 = 8$), these collision energies equate to 376 and 233 K, respectively. At the largest value of the kinetic temperature in their tabulations, $T = 300 \text{ K}$, $x = E/kT = 1.25$ and 0.78 , respectively. The values of the cross sections for larger values of x , required to converge the integral in equation (2), may be obtained by extrapolation, but such a procedure introduces uncertainties. The grid adopted here, which extends to $E = 4000 \text{ K}$, is sufficient to determine the rate coefficients reliably for temperatures up to about 400 K.

In table 4, we compare our calculations of the rate coefficients for the subset of transitions in CO involving levels $j_2 \leq 5$, induced by ortho-H₂ ($j_1 = 1$), with those of Mengel *et al* (2001). In this case, the rms deviation of the two sets of calculations is 7% at $T = 10 \text{ K}$, and 8% at 40 K. (Comparison with pre-publication results of Mengel *et al* revealed some

Table 4. A comparison of the rate coefficients (in units of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$) for de-excitation transitions between rotational levels j_2 of CO, induced by ortho-H₂ ($j_1 = 1$). The ‘scaled’ results were obtained on scaling the entire interaction potential by a factor of 0.93; see text, section 2.1.

Initial	Final	This work (unscaled)	This work (scaled)	Mengel <i>et al</i>
$T = 10 \text{ K}$				
1	0	0.388	0.387	0.305
2	0	0.596	0.565	0.535
3	0	0.105	0.090	0.070
4	0	0.083	0.073	0.050
5	0	0.015	0.013	0.011
2	1	0.730	0.690	0.637
3	1	0.842	0.795	0.798
4	1	0.159	0.139	0.113
5	1	0.124	0.110	0.082
3	2	0.801	0.723	0.703
4	2	0.862	0.807	0.858
5	2	0.188	0.160	0.128
4	3	0.827	0.760	0.750
5	3	0.896	0.844	0.884
5	4	0.871	0.774	0.692
$T = 40 \text{ K}$				
1	0	0.371	0.370	0.292
2	0	0.647	0.605	0.470
3	0	0.105	0.095	0.075
4	0	0.080	0.072	0.054
5	0	0.020	0.018	0.017
2	1	0.688	0.639	0.578
3	1	0.875	0.822	0.744
4	1	0.175	0.158	0.139
5	1	0.124	0.112	0.093
3	2	0.732	0.678	0.650
4	2	0.887	0.833	0.850
5	2	0.209	0.190	0.176
4	3	0.753	0.702	0.688
5	3	0.911	0.852	0.929
5	4	0.785	0.734	0.704

discrepancies, particularly at lower temperatures and for transitions from $j_2 = 5$. Subsequent investigation showed that, for certain transitions, the collision energy grid which they had used in the region near the threshold was insufficient to enable an accurate determination of the integral in equation (2) to be made.)

As discussed in section 2.1, we performed a duplicate set of calculations using an interaction potential scaled by a factor of 0.93. For collisions with ortho-H₂ ($j_1 = 1$), the rate coefficients computed using the scaled potential are given in table 4. When only the isotropic part of the interaction potential was scaled by this same factor, in the region of the potential minimum, the rate coefficients were found to differ by no more than 6% (and generally much less) from those obtained using the original potential, which was retained in subsequent calculations.

The complete set of computed rate coefficients, for $5 \leq T \leq 400$ K, is available from the CCP7 website (<http://ccp7.dur.ac.uk/>).

4. Concluding remarks

Cross sections have been computed using the quantum-mechanical-coupled-channels method, for rotational excitation of CO by H₂. We used a basis of levels of CO $j_2 \leq 29$, in the case of scattering on para-H₂ ($j_1 = 0$), and $j_2 \leq 20$, for scattering on ortho-H₂ ($j_1 = 1$). The H₂–CO interaction potential of Jankowski and Szalewicz (1998) was used. We found that shape resonances contribute significantly to the cross sections near the threshold, necessitating a fine collision energy grid when evaluating the rate coefficients at low temperatures. For transitions between low-lying levels of CO ($j_2 \leq 5$), the rate coefficients which we obtain agree well with the calculations of Mengel *et al* (2001), for collisions with para-H₂ and with their revised results for collisions with ortho-H₂.

If thermalized, molecular hydrogen would be mainly in its para form at very low temperatures. However, the timescale for ortho \leftrightarrow para thermalization in interstellar molecular clouds is sufficiently large, so that equilibrium may not be attained (Flower and Watt 1984). The fraction of ortho-H₂ might then be much larger than in equilibrium, and its contribution to the rotational excitation of CO would be significant.

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