Rate coefficients for rotationally inelastic collisions of CO with H_2

Markus Mengel, Frank C. De Lucia, and Eric Herbst

Abstract: We have performed quantum-scattering calculations to determine inelastic rate coefficients of the astrophysically important collision system CO–H_2. We have used a modified version of the most recent potential-energy surface by Jankowski and Szalewicz (J. Chem. Phys. **108**, 3554 (1998)), which has been proven to be superior to a previous potential surface by comparison with experimental pressure broadening data. In contrast to previous studies we find that inelastic rates with $\Delta J = 2$ for CO are smaller than those with $\Delta J = 1$.

PACS No.: 34.50Ez

Résumé : Nous avons calculé en théorie quantique des collisions les coefficients de taux inélastique dans les collisions CO–H_2 importantes en astrophysique. Nous avons utilisé une version modifiée de la plus récente surface d'énergie potentielle disponible publiée par Jankowski et Szalewicz (J. Chem. Phys. **108**, 3554 (1998)) qui a été démontrée supérieure aux surfaces antérieures en comparant avec les données sur l'élargissement des pics sous l'effet de la pression. Contrastant avec des études précédentes, nos résultats indiquent que les taux inélastiques pour $\Delta J = 2$ sont plus faibles que ceux pour $\Delta J = 1$.

[Traduit par la Rédaction]

1. Introduction

Inelastic rate coefficients for rotational population transfer of CO upon collisions with H_2 molecules are important parameters for modeling the conditions of dense interstellar clouds, where CO, an abundant and polar species, is the principal molecule used to map these objects [1]. For portions of clouds in which the rotational population of CO is not in thermal equilibrium, it is necessary to utilize inelastic rate coefficients for collisions with H_2, the dominant species, to determine the rotational-state populations of CO as functions of overall density and hence interpret spectroscopic observations. Since these rate coefficients are difficult to measure, scattering calculations based on an intermolecular potential surface are more suitable. Such calculations have been performed in a number of previous studies with a reasonable degree of agreement in most cases [2–4]. The calculations of Green and Thaddeus [2] were based on a potential for the CO–He interaction that had been modified by scaling factors to emulate the CO–H_2 potential. The works of Flower and Launay [4] and Schinke et.al. [3] were based on "true" CO–H_2 interaction potential surfaces obtained from quantum chemical calculations.

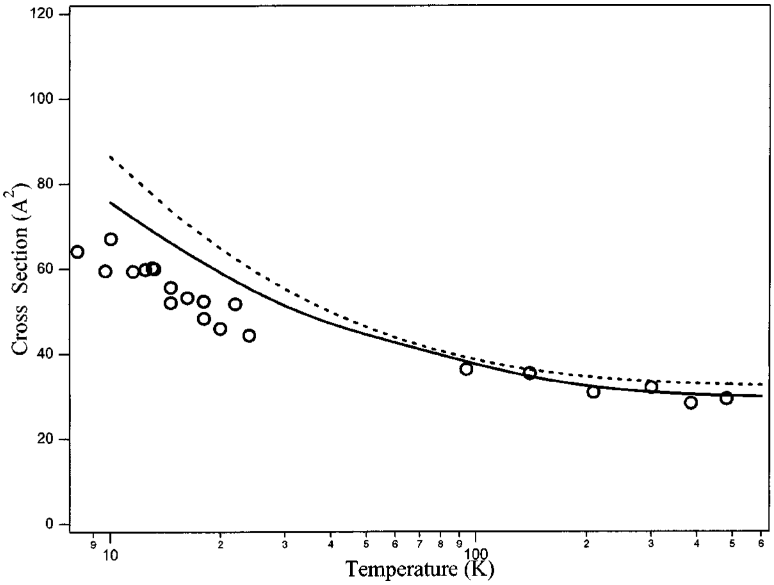
The motivation for presenting yet another calculation of these inelastic rates is twofold. First, very recently a new potential for the CO–H_2 interaction based on the symmetry-adapted perturbation theory (SAPT) method has been presented by Jankowski and Szalewicz [5], henceforth denoted the

Received July 20, 2000. Accepted December 12, 2000. Published on the NRC Research Press Web site on May 8, 2001.

M. Mengel, F.C. De Lucia, and E. Herbst. Department of Physics, The Ohio State University, 174 West 18th Ave., Columbus, OH 43210, U.S.A.

Can J. Phys **79**: 589–595 (2001) DOI: 10.1139/cjp-79-2/3-589

Fig. 1. Comparison of theoretical pressure broadening cross sections of the rotational CO transitions $J = 1 \leftarrow 0$ broadened by H_2 with a 3:1 ratio of ortho- and para-H_2. Calculations are based on two different potential-energy surfaces and use the coupled channel (CC) method. Continuous line: modified JS-potential (see text). Broken line: original JS-potential (ref. 5). Circles: experimental values.

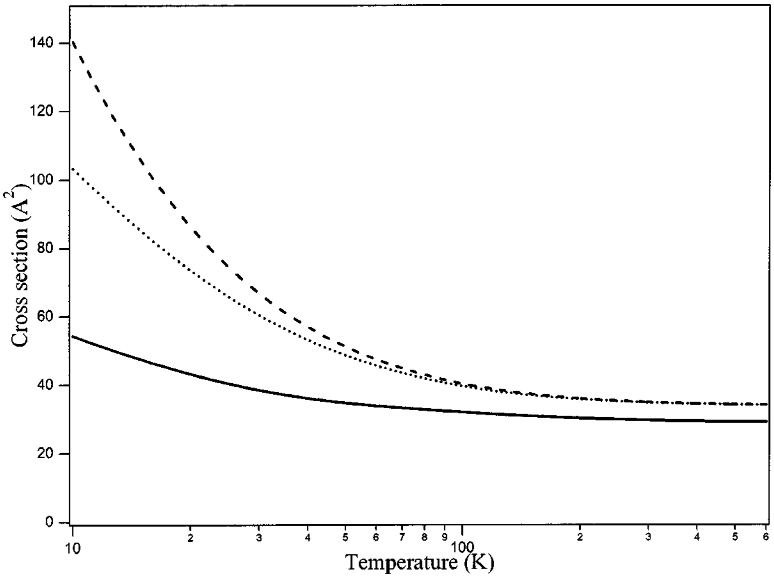


"JS-potential." Second, we have used this potential to calculate pressure-broadening parameters for low-J transitions of CO in collision with H_2 at temperatures between 8 and 600 K and compared the results to experimental values obtained with the collisional cooling method [6]. While the agreement between calculated and observed pressure-broadening parameters was not fully satisfactory at the lowest temperatures, this study involved the first experimental evaluation of a CO–H_2 potential surface at collision energies characterized as the domain of quantum collisions [7]. Furthermore, the agreement was better than that obtained with the potential by Schinke et al., which, before the JS-potential, had been deemed the best one available. In the present paper we will describe our quantum-scattering calculations of inelastic rate parameters for the CO–H_2 system, give an evaluation of both the JS and Schinke's potentials by means of their pressure-broadening results and compare our rate parameters to those of previous studies.

2. Quantum scattering calculations

Our previous calculations of pressure-broadening parameters [6] were done using the MOLSCAT computer code by Hutson and Green [8] and the original JS-potential [5]. We had originally planned to use this potential to calculate the inelastic cross sections of astrophysical interest as well. However, a study of second virial coefficients calculated from this potential [9] has shown that the attractive well of this ab initio potential-energy surface is too deep. A modification was, therefore, suggested by these authors; that is, multiplication by a factor of 0.93 for the purpose of virial coefficient calculation. We have applied this modification to recalculate pressure-broadening cross sections for the $R(0)$ transition of CO and found that the modified potential-energy surface in fact produces better agreement with the experiment. This can be seen in Fig. 1 where we compare calculated pressure-broadening cross sections based on the original and the modified JS-potential with experimental data. We, therefore, used the modified JS-potential to calculate inelastic state-to-state collisional cross sections. To comment on the

Fig. 2. Comparison of theoretical pressure broadening cross sections of the rotational CO transition $J = 1 \leftarrow 0$ broadened by para-H_2 ($J = 0$), based on different potential-energy surfaces. Continuous line: based on modified JS-potential (see text) and CC method. Dotted line: based on potential by Schinke et al. and CC method. Broken line: potential by Schinke et al. and CS approximation.



improved quality of these calculations over previous calculations, we compare our pressure-broadening results with those obtained from Schinke's potential using both the coupled channel (CC) method and the coupled states (CS) approximation. This comparison is visualized in Fig. 2 and shows a clear preference for the modified JS-potential. Since we were not able to apply the CS approximation to calculations of CO in collision with hydrogen in a rotational state higher than $J = 0$ with our version of the MOLSCAT code, we only compare results obtained with $J = 0$ hydrogen. Inclusion of the $J = 1$ states would generally lead to greater values of the cross section in all cases.

The implementation of the modified JS-potential into the MOLSCAT code was done by McBane [10]. The quantum-scattering calculations were performed using the CC method and the hybrid modified log-derivative Airy integrator [11] to solve the radial equations. The following rotational basis set of the CO molecule was used: $J = 0$–8 for collision energies from 0.5–50 cm^{-1}, $J = 0$–10 for collision energies from 50–170 cm^{-1}, and $J = 0$–16 for collision energies from 200–400 cm^{-1}. The rotational basis set of the H_2 molecule was $J = 0$ for para-H_2 and $J = 1$ for ortho-H_2. Due to negligible interconversion, para- and ortho-H_2 were treated in separate calculations. The following grid of collision energies was chosen: 0.5–25 cm^{-1} in steps of 0.5 cm^{-1}, 25–50 cm^{-1} in steps of 1 cm^{-1}, 50–170 cm^{-1} in steps of 5 cm^{-1}, 200–400 cm^{-1} in steps of 100 cm^{-1}. Pressure-broadening and inelastic cross sections were obtained as functions of kinetic temperature by calculating the thermal average (eq. 1 of ref. 6)

$$\sigma_{\mathrm{if}}(T) = \frac{1}{(kT)^2} \int \exp\left(\frac{-E}{kT}\right) \sigma_{\mathrm{if}}(E) E \, \mathrm{d}E \tag{1}$$

over this grid. Finally, thermally averaged inelastic cross sections σ_{if}, where “i” and “f” stand for the initial and final rotational states of CO, were transformed into rate constants R_{if} using (eq. 2.11 of ref. 2)

$$R_{\mathrm{if}} = \sqrt{\frac{8kT}{\mu\pi}} \sigma_{\mathrm{if}}(T) \tag{2}$$

Table 1. Rate constants (in units of 10^{-10} cm^3 s^{-1}) for all collisional downward transitions up to $J = 8$ of CO and para-H_2 ($J = 0$).

		T (K)					
$J_i \rightarrow J_f$		10	20	40	100	200	300
1	0	0.25637	0.27147	0.29220	0.32933	0.34540	0.36009
2	0	0.24144	0.26685	0.29201	0.32934	0.36279	0.39874
3	0	0.04726	0.05058	0.06145	0.09992	0.14265	0.17367
4	0	0.02079	0.02371	0.02916	0.04139	0.05086	0.05759
5	0	0.00542	0.00721	0.01129	0.02653	0.05081	0.07028
6	0	0.00189	0.00247	0.00373	0.00752	0.01290	0.01708
7	0	0.00091	0.00123	0.00211	0.00593	0.01349	0.01958
8	0	0.00030	0.00040	0.00061	0.00163	0.00359	0.00511
2	1	0.64428	0.60485	0.56940	0.60683	0.67801	0.74512
3	1	0.41755	0.44659	0.47034	0.51750	0.56619	0.62053
4	1	0.08675	0.09699	0.11695	0.18739	0.27997	0.35253
5	1	0.04224	0.04615	0.05381	0.07332	0.09279	0.10825
6	1	0.01177	0.01612	0.02401	0.05091	0.09620	0.13284
7	1	0.00488	0.00564	0.00782	0.01433	0.02486	0.03320
8	1	0.00244	0.00323	0.00479	0.01142	0.02421	0.03412
3	2	0.73442	0.65596	0.61612	0.66036	0.76031	0.85889
4	2	0.55350	0.56809	0.57521	0.60175	0.64616	0.70722
5	2	0.11007	0.12711	0.15299	0.22933	0.33181	0.41516
6	2	0.05366	0.06163	0.07165	0.09085	0.11185	0.13028
7	2	0.02210	0.02699	0.03729	0.06711	0.11758	0.15808
8	2	0.00833	0.00966	0.01199	0.01853	0.03030	0.03958
4	3	0.79325	0.72615	0.67077	0.68949	0.77742	0.87553
5	3	0.72139	0.70644	0.67641	0.66538	0.69600	0.75746
6	3	0.13235	0.16825	0.20088	0.27153	0.36945	0.45266
7	3	0.08381	0.08591	0.09421	0.10685	0.12539	0.14405
8	3	0.03555	0.04293	0.05412	0.08282	0.13529	0.17694
5	4	0.67199	0.65969	0.64791	0.69301	0.78124	0.87857
6	4	0.66817	0.72043	0.72234	0.70679	0.72959	0.79165
7	4	0.18290	0.21413	0.25137	0.31148	0.40555	0.48945
8	4	0.10408	0.11101	0.11769	0.11893	0.13645	0.15638
6	5	0.54593	0.67978	0.71389	0.73812	0.80880	0.90258
7	5	0.86253	0.84606	0.82368	0.75904	0.76471	0.82631
8	5	0.23004	0.27220	0.31124	0.34844	0.44150	0.52825
7	6	0.55286	0.69985	0.75982	0.76285	0.82964	0.92831
8	6	0.86491	0.91902	0.91636	0.78910	0.78809	0.85540
8	7	0.53758	0.74123	0.84633	0.80310	0.86411	0.96831

where T is the kinetic temperature, μ the reduced mass, and k the Boltzmann constant.

3. Results and summary

Tables 1 and 2 list thermally averaged inelastic rates for collisional downward transitions up to $J = 8$ of CO in collision with para-H_2 (Table 1) and ortho-H_2 (Table 2). Thermal averages were calculated at kinetic temperatures between 10 and 300 K. Inelastic upward rates can be obtained through the principle

Table 2. Rate constants (in units of 10^{-10} cm^3 s^{-1}) for all collisional downward transitions up to $J = 8$ of CO and ortho-H_2 ($J = 1$).

		T (K)					
$J_i \rightarrow J_f$		10	20	40	100	200	300
1	0	0.30454	0.28406	0.29244	0.34229	0.38285	0.42267
2	0	0.53474	0.50446	0.46997	0.44278	0.44878	0.48287
3	0	0.06976	0.07061	0.07470	0.10030	0.13932	0.17268
4	0	0.05008	0.05133	0.05357	0.05900	0.06534	0.07315
5	0	0.01062	0.01279	0.01698	0.02886	0.04727	0.06195
6	0	0.00539	0.00654	0.00850	0.01180	0.01664	0.02070
7	0	0.00205	0.00267	0.00393	0.00709	0.01258	0.01662
8	0	0.00097	0.00141	0.00165	0.00252	0.00419	0.00539
2	1	0.63689	0.61091	0.57824	0.62071	0.71643	0.81844
3	1	0.79774	0.78636	0.74372	0.70046	0.70790	0.76224
4	1	0.11309	0.12348	0.13882	0.19088	0.27080	0.33907
5	1	0.08196	0.08638	0.09297	0.10390	0.11932	0.13681
6	1	0.01955	0.02527	0.03447	0.05515	0.08928	0.11618
7	1	0.01187	0.01349	0.01687	0.02160	0.03117	0.03903
8	1	0.00524	0.00769	0.00903	0.01354	0.02241	0.02877
3	2	0.70266	0.67341	0.65038	0.69398	0.80494	0.92741
4	2	0.85821	0.87584	0.84984	0.80313	0.81064	0.87565
5	2	0.12846	0.15019	0.17623	0.23379	0.32305	0.40069
6	2	0.09326	0.10481	0.11642	0.12449	0.14264	0.16450
7	2	0.03221	0.03930	0.05128	0.07097	0.10873	0.13846
8	2	0.01857	0.02430	0.02604	0.02757	0.03808	0.04685
4	3	0.75004	0.71301	0.68802	0.72242	0.82813	0.95206
5	3	0.88436	0.93123	0.92864	0.87521	0.87937	0.95186
6	3	0.14131	0.18028	0.21863	0.26975	0.35912	0.43956
7	3	0.12490	0.13192	0.14469	0.14038	0.15952	0.18455
8	3	0.05045	0.07061	0.07828	0.08817	0.12620	0.15667
5	4	0.69232	0.69988	0.70387	0.73933	0.84301	0.96919
6	4	0.84860	0.96351	1.00391	0.93182	0.93611	1.02001
7	4	0.18437	0.22719	0.27748	0.30987	0.39900	0.48232
8	4	0.15233	0.19088	0.19360	0.15947	0.17943	0.20776
6	5	0.56928	0.68841	0.74794	0.76651	0.86904	1.00111
7	5	0.95087	1.03766	1.11074	0.97822	0.99223	1.09561
8	5	0.25010	0.35185	0.38054	0.35598	0.44485	0.53217
7	6	0.57436	0.73154	0.83945	0.80980	0.91228	1.05210
8	6	1.01183	1.32397	1.34900	1.03046	1.06040	1.18923
8	7	0.63753	0.94044	0.99948	0.84076	0.95871	1.11506

of detailed balance by multiplying the downward rates with the appropriate equilibrium fraction of upper and lower level population.

Tables 3 and 4 present a comparison of selected rate constants between our calculations and those of the three previous studies as discussed [2–4]. Rates of Table 3 were averaged at a temperature of 10 K, those of Table 4 at 40 K. There is generally reasonable agreement between our calculations and previous ones. However, our calculation does not predict rates with $\Delta J = 2$ to be larger than those with $\Delta J = 1$,

Table 3. Rate constants (in units of 10^{-10} cm^3 s^{-1}) for selected collisional transitions of CO and para-H_2 ($J = 0$) at a temperature of $T = 10$ K. Comparison with previous work.

J_i	$\rightarrow J_f$	This work	Ref. 3	Ref. 4	Ref. 2
1	0	0.256	0.238	0.230	0.176
2	0	0.241	0.378	0.350	0.276
3	0	0.047	0.042	0.028	0.044
4	0	0.021	0.044	0.038	0.026
5	0	0.005	0.014	0.006	0.004
2	1	0.644	0.561	0.280	0.351
3	1	0.418	0.641	0.620	0.480
4	1	0.087	0.089	0.050	0.054
5	1	0.042	0.084	0.072	0.058
3	2	0.734	0.676	0.250	0.370
4	2	0.554	0.785	0.740	0.610
5	2	0.110	0.130	0.063	0.055
4	3	0.793	0.566	0.320	0.372
5	3	0.721	0.865	0.890	0.682
5	4	0.672	0.496	0.400	0.260

Table 4. Rate constants (in units of 10^{-10} cm^3 s^{-1}) for selected collisional transitions of CO and para-H_2($J = 0$) at a temperature of $T = 40$ K. Comparison with previous work.

J_i	$\rightarrow J_f$	This work	Ref. 3	Ref. 4	Ref. 2
1	0	0.292	0.274	0.330	0.345
2	0	0.292	0.407	0.420	0.333
3	0	0.061	0.063	0.049	0.056
4	0	0.029	0.055	0.057	0.040
5	0	0.011	0.021	0.010	0.010
2	1	0.569	0.467	0.490	0.537
3	1	0.470	0.685	0.710	0.560
4	1	0.117	0.134	0.110	0.093
5	1	0.054	0.098	0.094	0.084
3	2	0.616	0.560	0.590	0.593
4	2	0.575	0.804	0.870	0.657
5	2	0.153	0.182	0.110	0.122
4	3	0.671	0.593	0.650	0.574
5	3	0.676	0.872	0.960	0.780
5	4	0.648	0.621	0.650	0.525

as in most of the previous results. Investigation of the inelastic cross sections as functions of collision energy showed that this was due to additional resonances in the low-energy area ($E \leq 20\,\mathrm{cm}^{-1}$) of the $\Delta J = 1$ transitions calculated with the modified JS-potential.

Acknowledgments

We wish to thank G.C. McBane for fruitful discussions and his programming work on the MOLSCAT code. Acknowledgment of support is made to the National Science Foundation, NASA, the Army Research Office, and the Ohio Supercomputer Center. M.M. acknowledges the Feodor-Lynen Fellowship awarded by the Alexander-von-Humboldt Foundation, Germany.

References

1. D.H. Hollenbach and H.A. Thronson, Jr. Interstellar processes, D. Reidel, Dordrecht, Boston. 1987.
2. S. Green and P. Thaddeus. Astrophys. J. **205**, 766 (1976).
3. R. Schinke, V. Engel, U. Buck, H. Meyer, and G.H.F. Diercksen. Astrophys. J. **299**, 939 (1985).
4. D.R. Flower and J.M. Launay. Mon. Not. R. Astr. Soc. **214**, 271 (1985).
5. P. Jankowski and K. Szalewicz. J. Chem. Phys. **108**, 3554 (1998).
6. M. Mengel, D.C. Flatin, and F.C. De Lucia. J. Chem. Phys. **112**, 4069 (2000).
7. C.D. Ball and F.C. De Lucia. Phys. Rev. Lett. **81**, 305 (1998).
8. J.M. Hutson and S. Green. MOLSCAT Version 12. Collaborative computational project No. 6 of the Science and Engineering Research Council, U.K. 1995.
9. J. Gottfried and G.C. McBane. J. Chem. Phys. **112**, 4417 (2000).
10. S. Antonova, A.P. Tsakotellis, A. Lin, and G.C. McBane. J. Chem. Phys. **112**, 554 (2000).
11. M.H. Alexander and D.E. Manolopoulos. J. Chem. Phys. **86**, 2044 (1987).