**Supplementary Information for**

**Rotational energy transfer in collisions between CO and Ar at temperatures from 293 to 30 K**

**Laura A. Mertens,a,b Hamza Labiad,a Otoniel Denis-Alpizar,c, d Martin Fournier,a David Carty,e Sébastien D. Le Picard,a Thierry Stoecklinc and Ian R. Simsa\***

aInstitut de Physique de Rennes, Département Physique Moléculaire, UMR 6251 du CNRS - Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France

bDivision of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

cInstitut des Sciences Moléculaires, Université de Bordeaux, CNRS-UMR 5255, 33405 Talence, France

dInstituto de Ciencias Químicas Aplicadas, Universidad Autónoma de Chile. El Llano Subercaseaux 2801, San Miguel, Santiago, Chile.

eDurham University, Joint Quantum Centre Durham-Newcastle, Departments of Physics and Chemistry, Lower Mountjoy, South Road, Durham, UK, DH1 3LE

# Supplementary Figure and Tables for Mertens et al.

**Supplementary Figure**



Figure S8 Legendre expansion coefficients *vl*(*R*) of the PES as a function of the intermolecular distance. The CO distance is fixed at its experimental value and the curves are labeled by the corresponding value of *l*.

Supplementary Tables

In the following Supplementary Tables S1 to S4, state-to-state rate constants for transfer between initial and final rotational states of CO in collision with Ar are reported for various temperatures under the conditions reported in the text. Experimental values are given with 2σ statistical errors and compared to theoretical values, which are given in parentheses. The sums of the experimental values of the state-to-state rate constants Σ*k*st-to-st (and the corresponding theoretical values in parentheses) are also given along with the total relaxation rate constants *k*Total as measured from the exponential decays and calculated via equation (1) (with the theoretical sum of all state-to-state rate constants out of the initial state given in parentheses).

Table S1. State-to-state rate constants for transfer between initial and final rotational states of CO in collision with Ar at ambient temperature (293 K) in units of 10-11 cm3 s-1.

|  |  |
| --- | --- |
| *J*final | *J*Initial |
| 0 | 1 | 4 | 6 |
| 0 | *J*Initial | - | - | - |
| 1 | 8.1 ± 3.5 (6.7) | *J*Initial | 1.5 ± 3.8 (2.3) | 1.4 ± 1.1 (1.7) |
| 2 | 3.4 ± 1.4 (7.4)  | 6.3 ± 3.6 (10.2) | 2.3 ± 2.0 (4.4)  | 1.3 ± 0.6 (1.5) |
| 3 | 5.6 ± 3.4 (5.6) | 7.8 ± 4.7 (8.2) | 6.7 ± 4.8 (6.7) | 2.1 ± 1.1 (3.4) |
| 4 | 2.6 ± 2.0 (4.0) | 2.9 ± 3.3 (5.9) | *J*Initial | 5.3 ± 1.4 (4.6) |
| 5 | 3.7 ± 3.1 (5.2) | 3.1 ± 5.3 (3.3) | 6.4 ± 2.9 (7.1) | 6.1 ± 1.6 (5.9) |
| 6 | 1.7 ± 2.8 (1.7) | 3.4 ± 3.1 (5.1) | 4.6 ± 8.4 (5.4) | *J*Initial |
| 7 | 4.7 ± 3.6 (3.4) | 1.2 ± 3.8 (1.5) | 3.5 ± 3.2 (4.1) | 4.1 ± 1.2 (5.7) |
| 8 | 1.6 ± 2.6 (1.2) | 1.8 ± 3.1 (3.1) | 2.4 ± 3.5 (2.0) | 3.8 ± 1.3 (4.0) |
| 9 | 1.0 ± 2.5 (1.8) | 1.2 ± 3.2 (1.2) | 1.9 ± 2.7 (2.5) | 3.0 ± 1.2 (3.1) |
| 10 | 1.0 ± 2.5 (0.9) | - | - | 1.7 ± 1.0 (1.5) |
| Σ*k*st-to-st | 33.4 ± 8.9 (37.9) | 27.8 ± 10.8 (38.5) | 29.4 ± 11.7 (34.5) | 28.9 ± 3.6 (31.3) |
| *k*Total | 38.6 ± 1.0 (40.2) | 40.0 ± 3.5 (46.7) | 39.8 ± 2.7 (39.4) | 34.8 ± 3.0 (35.6) |

Table S2. State-to-state rate constants for transfer between initial and final rotational states of CO in collision with Ar at 111 K in units of 10-11 cm3 s-1.

|  |  |
| --- | --- |
| *J*final | *J*Initial |
| 0 | 1 | 4 | 6 |
| 0 | *J*Initial | 2.6 ± 1.4 (3.6) | 0.7 ± 0.6 (6.9) | 0.6 ± 0.6 (0.3) |
| 1 | 11.6 ± 3.5 (8.3) | *J*Initial | 3.4 ± 1.8 (2.7) | 1.9 ± 0.8 (2.2) |
| 2 | 7.5 ± 1.8 (8.2)  | 9.8 ± 3.5 (8.4) | 6.4 ± 1.8 (4.9)  | 2.3 ± 0.9 (1.7) |
| 3 | 4.7 ± 1.6 (6.2) | 6.4 ± 1.8 (7.5) | 6.3 ± 1.3 (5.9) | 4.9 ± 1.8 (3.8) |
| 4 | 4.9 ± 1.8 (3.8) | 3.8 ± 2.2 (5.3) | *J*Initial | 3.5 ± 1.2 (4.7) |
| 5 | 4.1 ± 1.8 (4.7) | 3.1 ± 3.4 (2.6) | 3.9 ± 1.6 (5.4) | 4.1 ± 1.4 (5.3) |
| 6 | 1.5 ± 0.8 (1.2) | 1.7 ± 2.6 (3.4) | 3.9 ± 2.0 (4.0) | *J*Initial |
| 7 | 3.1 ± 1.8 (1.6) | 0.9 ± 1.6 (0.6) | 1.6 ± 1.8 (2.5) | 2.4 ± 0.9 (4.4) |
| 8 | 0.6 ± 2.5 (0.5) | 1.8 ± 3.4 (1.0) | 1.7 ± 1.7 (0.8) | 2.5 ± 1.3 (2.3) |
| 9 | 0.9 ± 3.4 (0.4) | 0.5 ± 2.3 (0.4) | 0.8 ± 1.5 (0.8) | 1.1 ± 1.2 (1.5) |
| 10 | - | - | - | 1.0 ± 1.3 (0.5) |
| Σ*k*st-to-st | 38.7 ± 6.8 (35.0) | 30.6 ± 7.7 (32.8)  | 28.6 ± 4.8 (33.9) | 24.3 ± 3.7 (26.6) |
| *k*Total | 38.0 ± 3.6 (35.3) | 29.7 ± 3.5 (33.2) | 27.3 ± 3.9 (34.2) | 28.1 ± 3.0 (27.2) |

Table S3. State-to-state rate constants for transfer between initial and final rotational states of CO in collision with Ar at 52 K in units of 10-11 cm3 s-1.

|  |  |
| --- | --- |
| *J*final | *J*Initial |
| 0 | 1 | 4 | 6 |
| 0 | *J*Initial | 1.8 ± 0.5 (3.5) | 0.5 ± 0.6 (0.8) | 0.4 ± 0.3 (0.3) |
| 1 | 7.5 ± 1.4 (8.8) | *J*Initial | 2.4 ± 1.0 (3.0) | 1.8 ± 0.4 (2.4) |
| 2 | 4.0 ± 1.0 (7.0)  | 6.1 ± 0.9 (7.1) | 4.3 ± 1.0 (5.6)  | 2.3 ± 0.5 (2.0) |
| 3 | 3.3 ± 1.3 (4.6) | 3.0 ± 0.9 (6.1) | 4.6 ± 1.5 (5.7) | 3.7 ± 0.8 (3.8) |
| 4 | 1.7 ± 1.5 (2.7) | 2.8 ± 1.1 (3.5) | *J*Initial | 2.6 ± 0.5 (4.7) |
| 5 | 1.8 ± 1.5 (2.4) | 1.0 ± 0.7 (1.4) | 3.3 ± 2.2 (3.9) | 2.9 ± 1.1 (5.2) |
| 6 | 0.5 ± 2.9 (0.4) | 0.7 ± 1.1 (1.3) | 1.4 ± 1.5 (2.2) | *J*Initial |
| 7 | 0.2 ± 2.1 (0.2) | - | 0.6 ± 1.3 (0.9) | 2.7 ± 1.5 (3.0) |
| 8 | - | - | - | 1.3 ± 2.5 (1.0) |
| Σ*k*st-to-st | 18.9 ± 4.7 (26.0) | 15.4 ± 2.2 (22.9)  | 17.1 ± 3.6 (22.0) | 17.8 ± 3.3 (22.6) |
| *k*Total | 24.1 ± 2.3 (26.0) | 18.1 ± 3.2 (23.1) | 21.4 ± 2.9 (22.3) | 23.2 ± 2.5 (23.1) |

Table S4. State-to-state rate constants for transfer between initial and final rotational states of CO in collision with Ar at 30.5 K in units of 10-11 cm3 s-1.

|  |  |
| --- | --- |
| *J*final | *J*Initial |
| 0 | 1 | 4 |
| 0 | *J*Initial | 5.0 ± 1.2 (3.6) | 0.9 ± 0.7 (1.0) |
| 1 | 5.4 ± 0.7 (8.8) | *J*Initial | 2.4 ± 1.2 (3.0) |
| 2 | 5.2 ± 1.0 (5.6)  | 5.2 ± 1.0 (6.1) | 5.8 ± 1.5 (5.8)  |
| 3 | 2.5 ± 1.5 (2.9) | 4.7 ± 1.2 (4.4) | 4.0 ± 1.7 (5.7) |
| 4 | 1.8 ± 1.3 (1.5) | 2.2 ± 1.4 (1.8) | *J*Initial |
| 5 | 0.5 ± 1.0 (0.8) | 0.5 ± 1.1 (0.6) | 2.6 ± 1.5 (2.7) |
| 6 | 0.3 ± 0.8 (0.1) | 0.7 ± 2.0 (0.3) | 1.1 ± 2.8 (0.9) |
| Σ*k*st-to-st | 15.6 ± 2.6 (19.7) | 18.4 ± 3.3 (16.8)  | 16.7 ± 4.2 (19.1) |
| *k*Total | 14.0 ± 2.9 (19.7) | 17.5 ± 4.1 (16.8) | 17.5 ± 2.9 (19.3) |