Comparative experimental and theoretical study of the rotational excitation of CO by collision with ortho- and para-D₂ molecules

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A joint crossed beam and quantum mechanical investigation of the rotationally inelastic collisions of CO with ortho- and para-D₂ molecules is reported. A new 4D potential energy surface (PES) averaged over the ground vibrational states of D₂ and CO is used to calculate the rovibrational bound states of the ortho-D₂ – CO complexes. Close coupling calculations are then performed in the rigid rotor approximation for ortho- and para-D₂ colliding with CO for the experimentally investigated transition of CO (j = 0 → 1) and for collision energies ranging from 0.1 to 25 cm⁻¹. The agreement between theory and experiment is found to be very good for both the bound state energies of the ortho-D₂ – CO complexes and for the inelastic scattering cross-sections showing that the free rotation of two rigid rotors is a very good model of the D₂ – CO system in this low collision energy domain.

1. Introduction

Because CO is the second most abundant molecule after H₂ in the interstellar medium (ISM), its collisions with H₂,²,⁴ and He⁵ have been extensively theoretically studied in recent years. CO is widely used as a tracer of physical conditions in galactic and extragalactic sources and such studies require knowing accurately the rates of the CO excitation and relaxation by inelastic collisions with H₂. The accuracy of the calculated rates depends critically on the quality of the potential energy surface (PES) used to perform the Close Coupling calculations. This is the reason why several models of the H₂–CO PES were developed⁶,⁷ with an increasing level of sophistication. Recently two full six-dimensional PESs were thus obtained¹,² and it was shown in particular that rigid-rotor calculations based on the vibrationally averaged PES (i.e. averaged over the vibrations of H₂ and CO) gave results almost indistinguishable from full-dimensional scattering calculations.¹ The quality of the PES in the study of Jankowski and coworkers was demonstrated by the excellent comparison with the experimental infrared and microwave spectra of the H₂–CO van der Waals complex.⁷ These experimental studies were the first performed in this domain of low collision energies where all the details of the PES appear in the structures of the cross-sections. In the present work we report a joint experimental and theoretical study of the D₂–CO rotationally inelastic collision for the same transitions in the [4–25] cm⁻¹ collision energy range. This study is complemented by the computation of the bound states of the ortho-D₂–CO (oD₂–CO) complex, which are compared to available experimental data.¹⁰ The D₂–CO and H₂–CO systems differ in many aspects such as their relative masses, the position of their center of mass and the values of the vibrational frequencies and the rotational constant of D₂ and H₂. The rotational constant and vibrational frequencies of D₂ are, for example, respectively, about one half and two third of those of H₂. Consequently, the new PES which is used here to describe the D₂–CO system is distinct from that used successfully for H₂–CO,⁷ as it is obtained by averaging the six-dimensional ab initio data⁷ over the ground vibrational wave functions of CO and D₂. This paper is organized as follows. In Section 2, the PES is presented and used to calculate the bound states of the oD₂–CO complex. A brief account of the parameters of the Close Coupling calculations is also given in the same section. The experimental part is presented in Section 3 and the comparison between theory and experiment is discussed in Section 4 while a few conclusions of this study are given Section 5.

2. Theory

A. Potential energy surface

In our previous studies of collisions of H₂ and CO, we used the 2012 four-dimensional interaction energy surface of H₂–CO.⁷
This surface is based on the 6D grid of ab initio points which are used to compute the interaction energies averaged over the particular vibrations of the H₂ and CO molecules. The resulting averaged energies are fitted to obtain the analytic representation of the 4D surface. Such an approach is an alternative to the averaging of the full-dimensional surface over the vibrational states of the fragments, but does not require the full-dimensional fit. Very recently, three of the authors of the present paper published a new 6D PES for H₂–CO, which could in principle be used for performing scattering calculations for D₂–CO. However, as the D₂–CO project was started before the 6D surface was ready, a new 4D PES based on the 6D ab initio data was specially designed for the present study. The vibrationally averaged energies have been calculated using the Taylor-expansion method, also employed for H₂–CO. Within this approach we need to know the averaged values of the H₂ and CO intramolecular distances and their squares. For the ground vibrational states of both molecules, if \( r \) and \( s \) denote the H–H and C–O distances, respectively, the corresponding values are found to be \( \langle r \rangle = 1.434562 \text{ Bohr}, \langle r^2 \rangle = 2.077687 \text{ Bohr}, \langle s \rangle = 2.13989 \text{ Bohr}, \) and \( \langle s^2 \rangle = 4.58320 \text{ Bohr}. \)

Since the bound-state and scattering calculations require an expansion of the angular dependence of the PES into products of spherical harmonics, the 4D CO–D₂ potential had to be refitted. The analytic fit was employed to generate interaction energies on a grid of 87,000 geometries in \( R, \theta_1, \theta_2 \) and \( \phi \), as in previous studies on H₂–CO where \( \theta_1 \) and \( \theta_2 \) are, respectively, the polar angles between the CO and DD interatomic distances and the \( R \) Jacobi vector while \( \phi \) is the Jacobi azimuthal angle. A total of 29 values of \( R \) (in Bohr) were thus used in the range [3.00–15.00]. This radial grid was combined with 3000 random angular geometries. The PES was refitted using a spherical harmonics expansion including all anisotropies up to \( l_1 = 10 \) for CO and \( l_2 = 6 \) for H₂ (where the integer indices \( l_1 \) and \( l_2 \) refer to \( \theta_1 \) and \( \theta_2 \) dependencies), resulting in 142 angular terms. The RMS residual was found to be lower than 0.1 cm⁻¹ for \( R > 5.00 \text{ Bohr} \).

The most significant terms were selected using a self-consistent Monte-Carlo estimator, resulting in a final set of 60 expansion functions with anisotropies up to \( l_1 = 7 \) and \( l_2 = 6 \). A cubic spline radial interpolation of the expansion coefficients was finally performed over the whole intermolecular distance range and was smoothly connected using a switching function to standard extrapolation (exponential and power laws at short-range and long-range, respectively). The resulting D₂–CO PES is very similar to the H₂–CO one as can be seen in Fig. 1. The global minimum energy of the new surface is \(-93.048 \text{ cm}^{-1}\) and is obtained for the linear arrangement \( \text{D–D} \cdot \cdot \cdot \text{C–O} \) and for an intermolecular distance \( R \) equal to 7.908 Bohr. The corresponding values for the H₂–CO complex are, respectively, equal to \(-94.096 \text{ cm}^{-1}\) and 7.911 Bohr. The values of the energies and intermolecular distances associated with the other linear geometry \( \text{H–H} \cdot \cdot \cdot \text{O–C} \) are also very close for the two systems. Their values are found to be \(-73.336 \text{ cm}^{-1}\) and 7.160 Bohr for D₂–CO and \(-73.738 \text{ cm}^{-1}\) and 7.168 Bohr for H₂–CO. The D₂–CO surface is then slightly shallower than the H₂–CO one by about 1.1% at the global minimum and 0.5% at the local one. We conclude from this comparison that the lower zero point energy of D₂ compared to H₂ and the small differences of the vibrationally averaged distances of these two molecules lead to only very small differences of the interaction energy surfaces. Also, the differences if any between the results involving these two systems will then result only from the differences between the diatom rovibrational
energies and wave functions and from those between the reduced masses and positions of the center of masses.

B. Bound state calculations
A first interesting test of the quality of the D₂–CO PES can be done by performing the calculations of the bound states of the system as they were experimentally determined recently. We use a close coupling approach to compute the rovibrational energy levels of the CO–D₂ complex using our didimat code according to the approach proposed by Danby and Hutson for the R-matrix and log-derivative propagators, respectively. Briefly, our code solves the rovibrationally inelastic Close Coupling equations in the space fixed frame using the Jacobi coordinates. The angular basis set is made of the usual coupled representation \(|j_{12}/M_e\rangle\) which provides eigenfunctions of the angular momenta \(j_{12} = j_1 + j_2\), \(\vec{l}\), \(j = j_1 + j_2 + l\) and of both \(j_1\) and the parity operator \(\Pi\), where \(j_1\) and \(j_2\) are the rotational angular momenta of H₂ and CO, \(\vec{l}\) is the relative angular momentum of the fragments, \(\vec{j}\) is the total angular momentum of the system and \(\vec{J}\) is its projection along the z space fixed axis. The vibrational levels of the van der Waals complex are calculated by performing calculations using a rigid rotor description of both D₂ and CO for all the values of the total angular momentum \(J\) and parity \(\varepsilon\) leading to bound states. We used the ground vibrationally averaged rotational constants for both molecules (\(B = 29.9037\) cm⁻¹ for D₂ and \(B = 1.9225\) cm⁻¹ for CO). The convergence of the bound levels of the CO–D₂ complex with respect to the CO and D₂ rotational basis was tested. Fifteen rotational states were included in the basis set describing the CO molecule while for \(\text{ortho-D}_2\) we included two rotational states. The maximum propagation distance was \(50\) Bohr. The calculations were performed for two values of the propagator step size (\(0.1\) and \(0.05\) Bohr) and the values of the bound state energies were obtained from a Richardson extrapolation as suggested by Hutson. The results of this approach are compared to the experimental results in the study of Potapov et al. in Table 1. As can be seen in this table the agreement between theory and experiment is found to be excellent with the maximum difference between the calculated and measured bound state energies of \(0.024\) cm⁻¹ and a global root mean square equal to \(0.008\) cm⁻¹. This result shows that the model of the free rotation of two rigid rotors suggested by Potapov et al. offers a good description of the D₂–CO system. If we now compare the bound states of the \(\text{oD}_2–\text{CO}\) complex to those calculated and measured for \(\text{pH}_2–\text{CO}\) we notice that the density of bound states is significantly higher for \(\text{oD}_2–\text{CO}\) than for \(\text{pH}_2–\text{CO}\). Since the PES is very similar, this result is a simple consequence of the change in the reduced mass of the two complexes.

C. Scattering calculations
The rigid rotor Close Coupling calculations were performed using our DIDIMAT code which was first applied to the H₂–HF collisions and used in our previous studies of H₂–CO, H₂–CS. This code solves the Close Coupling equations in the space fixed frame using \((R\text{-matrix})\) or a log derivative propagator. The \(T\) matrix elements are obtained and used to calculate the cross-sections for the transitions from an initial set of rotational levels of D₂ and CO labeled by the quantum numbers \((j_1 = j_\text{D}_2, j_2 = j_\text{CO})\) to a final set labeled by the quantum numbers \((j_1' = j_\text{D}_2', j_2' = j_\text{CO}')\):

\[
\sigma_{j_1,j_2\rightarrow j_1',j_2'} = \frac{\pi}{(2j_1 + 1)(2j_2 + 1)k_{j_1,j_2}} \sum_{J=0}^{\infty} (2J + 1) \sum_{J_1=-j_1}^{j_1} \sum_{J_2=-j_2}^{j_2} \sum_{J'=J_2-J_1}^{J_2} \sum_{J'=J_2-J_1}^{J_2} \left| T_{j_1,j_2;j_1',j_2'}^{J,J'} \right|^2
\]

The magnitude of the wave vector is defined by \(k_{j_1,j_2} = \frac{2\mu}{\hbar^2}(E - \epsilon_{j_1,j_2})\), with \(\epsilon_{j_1,j_2}\) being the eigenenergy associated with a given set of initial rotational state \((j_1,j_2)\) of D₂ and CO, \(E\) the total energy and \(\mu\) the relative mass of the system.

Full Close Coupling calculations were performed using the rigid rotor approximation for collision energies ranging from \(10^{-2}\) to \(50\) cm⁻¹ and with the rotational constants given in the Bound state calculations section. The rotational basis set was the same as the one used for the bound state calculations. The propagation along the intermolecular coordinate was carried out using the log derivative propagator and a step size of \(0.1\) a₀. The convergence of the cross-sections as a function of the maximum intermolecular distance and the total angular momentum was checked for each collision energy. The minimum propagation distance was \(2.8\) a₀ while the maximum propagation distance was always greater than or equal to \(50\) a₀.

3. Experimental
The integral cross-section (ICS) for collisional excitation of CO by \(\text{para-H}_2\) and \(\text{normal-H}_2\) has been observed for the \(j = 0 \rightarrow 1\) and \(0 \rightarrow 2\) transitions. Using the same apparatus as the one described in the previous study, we measured the ICS corresponding to the CO \(j = 0 \rightarrow 1\) excitation induced by collisions with \(\text{ortho-}\) and \(\text{normal-D}_2\). The collision induced population enhancement of the \(j = 1\) level was probed as a function of the collision energy using the \((2 + 1)\) resonance-enhanced
multiphoton ionisation via the \((E^1 \Pi, v = 0 \leftrightarrow X^1 \Sigma^+ g^+, v = 0)\) transition at 46474.8 cm\(^{-1}\) \((215.17 \text{ nm})\).\(^{20}\) The initial residual population at the \(j = 1\) level was offset by shot-to-shot background subtraction when triggering the probe laser and the CO beam at 10 Hz with the \(D_2\) beam at 5 Hz. The ICSs were recovered from the measured intensities \(I_{\text{REMPI}}\):

\[
\text{ICS} \propto \frac{I_{\text{REMPI}}}{v_r \langle T_i \rangle},
\]

(1)

where \(v_r\) stands for the relative velocity and \(\langle T_i \rangle\) for the mean interaction time.

The relative translational energy reads:

\[
E_T = \frac{1}{2} \mu v_r^2 = \frac{1}{2} \mu (v_1^2 + v_2^2 - 2 v_1 v_2 \cos \chi)
\]

(2)

where \(\mu\) and \(v_i\) \((i = 1, 2)\) are the reduced mass and the velocities of the collision partners, respectively. The mean crossing angle, \(\chi\), generally differs from the actual beam axis angle, \(\chi_0\) for reasons discussed in the ESI of ref. \(^{21}\). Briefly, it was shown that for nearly thermo-neutral processes, the detected species propagate almost in phase with the reactants, with two consequences. First, the mean crossing angle \(\chi\) is shifted from the beam axis angle \(\chi_0\), with \(\Delta \chi = \chi - \chi_0\); this shift and the crossing angle spread \(\delta \chi\) both depend upon the beam axis angle, as shown in Fig. 2a. Second, the interaction time increases at decreasing crossing angles. This effect is more pronounced when using beams of matched velocities and for heavy–light collisions, which is the case here. The energy resolution (which depends on velocity and crossing angle spreads) and mean interaction time as a function of collision energy are displayed in Fig. 2b. These effects are detailed for the \(O_2 + H_2\) inelastic collisions in the supplementary materials of ref. \(^{21}\).

4. Results and discussion

(a) Theory

The results of Close Coupling calculations are presented in Fig. 3 and 4 for the rotational excitation of CO \((j_{\text{CO}} = 0 \rightarrow 1)\), respectively, in collisions with \(oD_2\) and \(pD_2\). The partial wave expansions of these cross-sections are also represented in the

![Fig. 2](image-url)  
(a) Crossing angle shift (upper panel) and spread (lower panel). (b) Mean interaction time for all experimental sets (upper panel) and energy resolution (lower panel).

![Fig. 3](image-url)  
Fig. 3 Partial wave expansion of the CO \((j = 0 \rightarrow 1)\) rotational excitation cross-section in collisions with \(oD_2\) as a function of the collision energy. The curves are labeled by the value of the total angular momentum quantum number \(J\).
same figures. Many shape and Feshbach resonances appear in these two figures. The density of the resonances is larger than for the collisions of \( p\text{H}_2 + \text{CO} \) as was noticed in the previous paragraph for the density of the bound states of \( o\text{D}_2–\text{CO} \) compared to those of \( p\text{H}_2–\text{CO} \). This is mainly due to the change in the relative mass which is almost doubled when one moves from \( \text{H}_2–\text{CO} \) to \( \text{D}_2–\text{CO} \), thus requiring more partial waves to get the convergence of the cross-sections. Also, if at low collision energy it is often possible to attribute a single partial wave to a given resonance, this task becomes more and more difficult at higher energy.

The results of our Close Coupling calculations are then compared in Fig. 5 and 6 for the rotational excitation of \( \text{CO} \) \((j = 0 \rightarrow 1)\) in collisions with \( o\text{H}_2 \) and \( p\text{D}_2 \) as a function of collision energy.

(b) Experiment

The comparison between experiment and theory for the \( \text{CO} \) \((j = 0 \rightarrow 1)\) excitation by collisions with \( o\text{tho}\text{o}–\text{D}_2 \) is displayed in Fig. 7. In a similar manner the results obtained for \( \text{CO} \)
were fitted to Gaussian functions, with peak positions \(\gamma_0\) and \(\gamma_1\), yielding the peak velocities \(v = dl/(t_1 - t_0)\), and the velocity spreads \(\delta v\text{HWHM}\) from the pulse broadening. \(\nu\) Speed ratio \(S = v/\delta v\text{HWHM}\) (Gaussian limit of the Maxwell–Boltzmann distribution). \(\tau\) Pulse width \(\tau\text{HWHM}\) at the crossing point. \(\tilde{\sigma}\) Angular divergence (HWHM).

### Table 2. Characteristics of the molecular beams used in the determination of the integral cross-sections

<table>
<thead>
<tr>
<th>Beam</th>
<th>Gas mixture</th>
<th>(T_a^a) (K)</th>
<th>(\nu^b) (ms(^{-1}))</th>
<th>(\delta v\text{HWHM}^b) (ms(^{-1}))</th>
<th>(S^c)</th>
<th>(\gamma_0^d)</th>
<th>(\delta v)^e</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 CO</td>
<td>CO:0.004/Ne:0.996</td>
<td>230</td>
<td>697 ± 5</td>
<td>19.8</td>
<td>≥35</td>
<td>28.3</td>
<td>0.9</td>
</tr>
<tr>
<td>#2 n-D(_2)</td>
<td>Neat</td>
<td>25</td>
<td>763 ± 5</td>
<td>46.5</td>
<td>≥13</td>
<td>14.4</td>
<td>2.0</td>
</tr>
<tr>
<td>#3 n-D(_2)</td>
<td>Neat</td>
<td>10</td>
<td>728 ± 5</td>
<td>48.6</td>
<td>≥15</td>
<td>16</td>
<td>2.0</td>
</tr>
<tr>
<td>#4 o-D(_2)</td>
<td>Neat</td>
<td>10</td>
<td>732 ± 5</td>
<td>43.5</td>
<td>≥16</td>
<td>14</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\(a\) Temperature set point of the cold head. \(b\) Peak velocities, \(v\), and velocity spreads, \(\delta v\text{HWHM}\), are deduced from temporal profiles recorded at the crossing point (detecting CO by REMPI and D\(_2\) by CO signal depletion), and at a distance \(d = 393.3\) mm downstream (with a fast-ionization gauge inserted perpendicular to the molecular beam). Both profiles were fitted to Gaussian functions, with peak positions \(t_0\) and \(t_1\) and half-width at \(1/e\) (HWHM), \(\gamma_0\) and \(\gamma_1\), yielding the peak velocities \(v = dl/(t_1 - t_0)\), and the velocity spreads \(\delta v\text{HWHM}\) from the pulse broadening. \(c\) Speed ratio \(S = v/\delta v\text{HWHM}\) (Gaussian limit of the Maxwell–Boltzmann distribution). \(d\) Angular divergence \(\tilde{\sigma}\).

**5. Conclusion**

A joint experimental and theoretical study of the CO \(j = 0 \rightarrow 1\) inelastic cross-section in collision with D\(_2\) was presented. The new 4D PES obtained by averaging the original model of Jankowski \textit{et al.}\(^7\) over the vibrational level of D\(_2\) was shown to differ only slightly from the one averaged over the vibrational level of H\(_2\). The present results were compared with those obtained previously for the collisions of H\(_2\) with CO.\(^4\) The cross-sections for the rotationally inelastic transition of CO \(j = 0 \rightarrow 1\) in collisions with D\(_2\) were found to be always greater than those involving H\(_2\). This result was shown to be essentially due to the ratio of the relative masses of these two collisional systems which is roughly equal to two. More partial waves are then needed to converge the cross-sections involving D\(_2\) and these supplementary contributions increase significantly the magnitude of the cross-sections. The agreement between theory and experiment is found to be excellent and demonstrates the validity of the rigid rotor approximation for this system in this domain of collision energy. The computed bound state energies of the o-D\(_2\)-CO were also found to be in excellent agreement with the available experimental data in the study of Potapov \textit{et al.}\(^10\) showing that the model of the free rotation of two rigid rotors suggested by Potapov \textit{et al.}\ offers a good description of the D\(_2\)-CO system. In other words CO and D\(_2\) are so weakly bound that they almost freely rotate independently. The results presented here for the benchmark D\(_2\)-CO system demonstrate that theory and experiment have reached a high level of refinement. Just like bound states, inelastic cross-sections can now be probed with spectroscopic resolution and they provide very useful and complementary information on the interactions between individual molecules.

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