Communication: Rotational excitation of HCl by H: Rigid rotor vs. reactive approaches
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I. INTRODUCTION

HCl molecules can be considered as prototypes for the inelastic collision studies of diatomic species. Indeed, their large rotational energy level spacings make them well suited for state resolved scattering experiments as well as for quantum scattering calculations. Ro-vibrational energy transfer in HCl due to collisions with rare gas and small molecules has been the object of constant and detailed attention. From the astrophysical point of view, HCl is also of particular interest. It was first identified by Blake et al. in the Orion Molecular Cloud 1, and the HCl lines are frequently used to trace dense gas of the interstellar medium (ISM). HCl was also predicted to be an important reservoir of interstellar chlorine, especially in the dense regions of the ISM. However, recent observations have shown that this may not be the case and that chlorine is probably in other species than HCl. Accurate determination of HCl abundance is then crucial to understand and constraint the interstellar chlorine chemistry.

Proper determination of the HCl abundance in the ISM relies on collisional data with the most abundant species that are usually the H$_2$ molecule, the He and H atoms and electrons. Without these collisional rate coefficients, only approximate estimates of the molecular abundance are possible assuming local thermodynamic equilibrium (LTE), which is generally not a good approximation.

Rate coefficients for the rotational excitation of HCl by He atoms were calculated by Neufeld and Green several years ago and revisited recently. HCl–H$_2$ rate coefficients were computed recently by Lanza and co-workers. To the best of our knowledge, no collisional data exist for collisions with H whereas HCl was detected in diffuse molecular clouds and in photon-dominated regions (PDRs) of the ISM where H is very abundant. It is then crucial to extend the rate coefficient calculations to the H collisional partner.

Inelastic collisions between HCl and H are much more difficult to study than collisions between HCl and He. Indeed, during a collision between HCl and H, three processes can occur and compete.

1. The inelastic process:

   \[ \text{HCl}(v,j) + \text{H} \rightarrow \text{HCl}(v',j') + \text{H}. \]  

2. The reactive process:

   \[ \text{HCl}(v,j) + \text{H} \rightarrow \text{Cl}(v',j') + \text{HH}. \]  

3. The exchange process:

   \[ \text{HCl}(v,j) + \text{H} \rightarrow \text{HCl}(v',j') + \text{H}. \]  

Here, $v$ and $j$ denote the vibrational and rotational levels of the diatomic molecules, respectively.

The HCl + H ↔ Cl + H$_2$ reaction is a benchmark for triatomic abstraction reactions. Accurate theoretical studies were enabled by the availability of high-quality potential energy surfaces (PESs). Surprisingly, the HCl + H inelastic collisions have received less attention and the available data only concern the exchange process.

Because of the activation barrier that inhibits the reactive and the exchange processes at low collisional energies, inelastic collisions are expected to be the dominant process at typical interstellar temperatures ($T < 500$ K). It is then crucial to provide state-to-state data for this process. Nevertheless, even if inhibited by a barrier, the HCl + H → Cl + H$_2$ reaction is exothermic and can proceed through tunneling at moderate temperatures. Accurate determination of pure rotational excitation cross sections may have then to be obtained from approaches that include the reactive channels.

In this communication, we study the rotational excitation of HCl by H using an exact quantum three dimensional...
(3D) approach including the reactive channels. The results are compared to rigid rotor calculations, so that we try below to determine the validity of neglecting the reactive channels in the study of inelastic collisions for a reactive (through a barrier) system. The paper is organized as follows: Sec. II provides a brief description of the scattering calculations. In Sec. III, we present the results and we compare them to rigid rotor results in Sec. IV. Concluding remarks are drawn in Sec. V.

II. SCATTERING CALCULATIONS

In our investigation of the scattering dynamics, we use the CH$_2$ global PES of Bian and Werner. The \textit{ab initio} CH$_2$ PES has been calculated at the internally contracted multireference configuration interaction (MRCI)\textsuperscript{25} level using large atomic basis set.

We used the ABC reactive scattering code\textsuperscript{25} to carry out close coupling calculations for all values of the total angular momentum that made a non-zero contribution to inelastic, exchange, and reactive processes. As discussed in Tao and Alexander,\textsuperscript{26} it is computationally efficient to choose basis functions which are eigenfunctions of the operator corresponding to interchange of the two hydrogens. Since the Hamiltonian is symmetric with respect to interchange of the two hydrogens, there will be no coupling between odd (ortho) and even (para) rotational states of H$_2$, so that the number of coupled channels is reduced by a factor of $\frac{1}{2}$. Then, we obtain inelastic, reactive, and exchange cross sections following the methodology described in Ref. 26. We calculated the cross sections involving the $1^1$ first rotational levels of HCl.

We refer hereafter to these calculations as 3D calculations. While excited vibrational states are included in the calculation to ensure convergence, cross sections are reported only for rotational excitations of HCl in its ground vibrational state.

We also performed calculations for pure rotational excitation of HCl by H using the rigid rotor approximation. Two series of calculations were performed. First, we have chosen to fix the HCl internuclear separation at a value of $r_{HCl} = 2.43$ a$_0$, the ground state vibrationally averaged value. Second, we have averaged the 3D PES with a vibrational ground-state wavefunction of HCl. HCl vibrational wave functions were evaluated by the Fourier grid Hamiltonian method\textsuperscript{27} from a HCl potential calculated with a RKR program.\textsuperscript{28}

In both set of rigid rotor calculations, the standard time-independent coupled scattering equations were solved using the MOLSCAT code.\textsuperscript{29} We refer hereafter to these calculations as two dimensional (2D) and two dimensional average (2Da) calculations, respectively.

III. RESULTS

Using the computational scheme described above, cross sections for the inelastic, reactive, and exchange processes were computed for total energy up to 4000 cm$^{-1}$. Figure 1 displays the energy variation of the integral cross sections obtained with the 3D approach for the inelastic, reactive, and exchange processes for collisions of HCl($j = 0$) and HCl($j = 1$) with H.

At low collisional energies, the reactive and exchange processes are negligible. Such findings could be anticipated considering the activation barrier for the two processes (1800 and 6300 cm$^{-1}$, respectively\textsuperscript{21}). When the collisional energies increase, the reactive process can take place and compete with the pure rotational excitation. However, we note that the magnitude of the reactive cross sections remains low compared to that of the rotational excitation. Over all the collisional energies range explored in this work, the exchange process remain negligible compared to the others processes.

Then, we focus on the collisional excitation process and we sum the inelastic and exchange cross sections to obtain state-to-state observable data. Figure 2 displays the energy variation of the cross sections for the rotational excitation of HCl($j = 0$) and HCl($j = 1$) by H.

As expected, the cross sections decrease with increasing $\Delta j$. The strongest collision-induced rotational HCl transitions are the transitions with $\Delta j = 1$. More generally, we observe propensity rules in favor of transitions with odd $\Delta j$ because of the strong anisotropy of the H–H PES with respect to the H approach. The magnitude of the HCl-H inelastic cross sections is of the same order as the HCl-H$_2$ ones\textsuperscript{5} so that we can expect that collisional excitation by H will clearly compete...
with collisional excitation by H$_2$ in astrophysical media where both H and H$_2$ are abundant.

IV. COMPARISON WITH RIGID ROTOR RESULTS

Figure 3 shows the integral cross sections for rotational excitation of HCl by H obtained using the rigid rotor approximations (both 2D and 2Da) and the 3D approach.

One can observe a very good agreement between the three sets of data over all the energy range considered in this work. Such agreement could certainly have been anticipated and can be explained by the low magnitude of the reactive cross sections. Indeed, the reactive process is very weak and does not significantly impact the pure collisional excitation. Hence, at low and moderate collisional energies, rigid rotor and 3D results are in good agreement, the agreement between 2Da and 3D results being even almost perfect. At high collisional energies, both rigid rotor cross sections slightly overestimate the 3D cross sections.

Two obvious reasons can explain these differences.

(i) The 2D approaches do not take into account the vibration of HCl in the scattering calculations.

(ii) The 2D approach neglects the reactive channels.

As discussed above, at kinetic energies larger than 2000 cm$^{-1}$, the reaction starts to (slightly) compete with the inelastic process since the H and HCl reactants have enough energies to pass the barrier. This explains why the rigid rotor approaches, both of which neglect the reactive pathway, slightly overestimate the cross sections for the inelastic process.

Vibrational effect may also be important for the rotational excitation of light hydride molecules$^{30}$ for which the anisotropy of the PES is large with respect to intermolecular distance. However, averaging the PES over the ground vibrational wavefunction generally allows to correct the effect. In our case, the 2Da cross sections are in better agreement with the 3D cross sections than the 2D cross sections showing that vibrational effect have been correctly considered by averaging the PES over the HCl ground vibrational wavefunction. Hence, we can conclude that the differences at high collisional energies come mainly from the non-inclusion of reactive channels in the rigid rotor approaches.
V. CONCLUSION

We have presented quantum mechanical calculations of cross sections for the rotational excitation of HCl by H, including the Cl + H₂ reactive channels using the PES of Bian and Werner. Additional calculations were performed within the rigid rotor approximation and the different sets of inelastic cross sections were compared. It is found that an accurate description of the rotational excitation of HCl by H is obtained using the rigid rotor approach at low collisional energies. At higher energies, the effects of reactive channels become negligible. We also found that, when using the rigid rotor approach, it is safer to use a PES averaged over the vibration of the diatomic molecules than a PES obtained for a fixed intermolecular distance.

From this work, it seems that studies of rotational excitation of interstellar species with H or H₂ can be treated using the rigid rotor approach even if the system is reactive, provided that the reaction proceeds through a barrier and that we consider low collisional energies. Such results confirm the conclusion of Lique and Faure on the H + D₂ collisional system. Hence, it will be, for example, easy to provide data for the interstellar HF molecules in collisions with H. The present study also validates previous pure collisional excitation studies on reactive system like OH–H₂ or CN–H₂.

Finally, the new collisional cross sections can be used to accurately determined the HCl abundance in astrophysical media where H is abundant. The magnitude of the HCl–H₂ cross sections being relatively large, we can anticipate a similar impact to that of HCl–H₂ cross sections on the astrophysical modelling (i.e., a significant lowering of the HCl abundance or CN–H₂ reactive channels using the PES of Bian and Werner).

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28. RRK1 is R. J. Le Roy’s program for applying the first-order Rydberg-Klein-Redlick procedure to spectroscopic constants for a diatomic molecule to determine its potential energy function. See http://scicenter.uwaterloo.ca/~devoor/rrk/.