We report rotational quenching cross sections and rate coefficients of HCl due to collisions with He. The close-coupling method and the coupled-states approximation are applied in quantum-mechanical scattering calculations of state-to-state cross sections for HCl with initial rotational levels up to \( j = 20 \) for kinetic energies from \( 10^{-5} \) to \( 15,000 \text{ cm}^{-1} \). State-to-state rate coefficients for temperatures between 0.1 and 3000 K are also presented. Comparison of the present rate coefficients with previous results reported in the literature for lowly excited rotational levels shows reasonable agreement. Small differences are attributed to the differences in the interaction potential energy surfaces. The uncertainty in the computed cross sections and rate coefficients is estimated by varying the potential well depth. Applications of current results to astrophysical systems are also briefly discussed.

**Key words:** ISM: molecules – molecular data – molecular processes

*Online-only material:* color figures

1. INTRODUCTION

Molecular collisional excitation rate coefficients are important as they contribute to level excitation (and quenching or deexcitation) in competition with radiative processes. In cold environments such as the interstellar medium (ISM), the dominant collision partners are often H\(_2\) and He, except in photodissociation regions and diffuse gas where collisions with electrons and H can become important. Precise laboratory data including collisional (de)-excitation rate coefficients are required, for a range of temperatures, to interpret the complicated interstellar spectra of molecular gas not in local thermodynamic equilibrium (LTE). Because of the complexity and difficulty in direct measurements, only limited state-to-state collision rate coefficients have been obtained for systems of astrophysical interest (see, for example, Carty et al. 2004). Therefore modeling astrophysical systems rely heavily on theoretical estimates (Flower 2007; Dubernet et al. 2009; Lique et al. 2009; Daniel et al. 2011; Klos & Lique 2012; Faure & Lique 2012; Lique & Alexander 2012; Wiesenfeld & Faure 2013; Roueff & Lique 2013; Yang et al. 2013; Dubernet et al. 2013).

Here we consider the hydrogen halide HCl, which has been detected in the atmospheres of some planets, as well as in interstellar clouds (Blake et al. 1985; Salez et al. 1996; Bahou et al. 2001). It is an important tracer of chlorine and can be used to constrain the chlorine elemental abundance and isotope ratios. Zmuidzinas et al. (1995) observed it toward the Sagittarius B2 complex and modeled its non-LTE spectrum. Further, HCl was recently detected in the circumstellar envelope of IRC+10216 by Herschel (Cernicharo et al. 2010). It has also been surveyed throughout the ISM via its rotational line emission by Peng et al. (2010). It appears that HCl is a particularly good tracer of molecular cloud cores of the highest density; however, the density estimates are limited by the uncertainty in collision rates.

The HCl–He collision system has been investigated theoretically and experimentally in a variety of studies (Green & Nesbitt 1990). Murdachaew et al. (2004) also pointed out that the dissociation energy predicted by the SAPT potential is in good agreement with the semiempirical PES of Willey et al. (1992) predicting that the global minimum is on the Cl side. The accuracy of the SAPT potential was tested by performing rovibrational bound states calculations of the HCl–He complex, which show that the calculated transition frequencies were in excellent agreement with the measurements of Lovejoy & Nesbitt (1990). Murdachaew et al. (2004) also pointed out that the dissociation energy predicted by the SAPT potential for the complex is probably more accurate than the experiment. Fajin & Fernandez (2006) presented another two-dimensional HCl–He potential using the coupled cluster with single, double, and triple excitations (CCSDT) method. This potential is very similar to the SAPT PES, but gives better agreement with the experimental dissociation energy and rotational energy levels of the HCl–He complex. Very recently three-dimensional and two-dimensional PESs, which used the supermolecular approach based on the CCSD(T) method, but at different levels of theory, were presented by Lanza & Lique (2012) and by Ajili et al. (2013). These new potentials were also used in CC calculations of pure rotational excitation of HCl by He by these authors. Cross sections for transitions among the first 11 rotational states of HCl were calculated for total energy of up to 3000 cm\(^{-1}\) using MOLSCAT with the log-derivative propagator of Manolopoulos (1986). Rate coefficients were presented from 5 to 300 K.
In this work, we performed explicit quantum scattering calculations of rotational quenching of HCl by He to higher levels of rotational excitation using the SAPT potential of Murdachaew et al. (2004). HCl–He rate coefficients are presented for a large range of temperature (0.1–3000 K) which will aid in modeling rotational spectra of HCl in various astrophysical and atmospheric environments. We discuss the computational method in Section 2 and the results in Section 3. In Section 4, an estimate of the uncertainty in the cross sections and rate coefficients is presented, while Section 5 briefly discusses application of the current results to astrophysics.

2. COMPUTATIONAL METHOD

The theory developed by Arthurs & Dalgarno (1963) for atom–diatom scattering is adopted. HCl was treated as a rigid rotor with bond length equal to the equilibrium distance $r_e = 1.275$ Å. The calculations presented here were performed by applying the CC method and the CS approximation (see, for example, Flower 2007). The HCl–He interaction potential is expressed by $V(R, \theta)$, where $R$ is the distance from the HCl center of mass to the He atom, and $\theta$ is the angle between $R$ and the HCl molecular axis, with $\theta = 180^\circ$ defined for the collinear arrangement He–H–Cl. The potential $V(R, \theta)$ was expanded in the form

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{\text{max}}} v_\lambda(R) P_\lambda(\cos\theta),$$

where $P_\lambda$ are the Legendre polynomials and $v_\lambda(R)$ the expansion coefficients of the potential.

For a transition from an initial rotational state $j$ to a final rotational state $j'$, the integral cross section can be expressed in terms of the scattering matrix $S$, within the CC formalism by

$$\sigma_{j \rightarrow j'}(E_j) = \frac{\pi}{(2j+1)k^2_j} \sum_{J=0}^{j} (2J + 1) \times \sum_{J'=|j-j'|}^{J+J'} \left| S_{jJ'}(E_j) \right|^2,$$

where the total angular momentum $J = l + j$ is composed of the rotational angular momentum $j$ of the HCl molecule and the orbital angular momentum $l$ of the collision complex, $k_j = \sqrt{2\mu E_j}/\hbar$ is the wave vector for the incoming channel, $E_j$ the center-of-mass kinetic energy for the incoming channel corresponding to the initial rotational state $j$ of HCl, and $\mu$ the collision system reduced mass.

All reported scattering calculations were performed using the quantum-mechanical scattering code MOLSCAT (Hutson & Green 1994). The propagation was carried out from an intermolecular separation $R = 1.0$ to $R = 100$ Å. To ensure the accuracy of the state-to-state rate constants for temperatures from $10^{-4}$ to 3000 K, kinetic energies between $10^{-5}$ cm$^{-1}$ and 15,000 cm$^{-1}$ were used in our state-to-state cross section calculations. The angular dependence of the interaction potential was expanded in Legendre polynomials shown in Equation (1) with $\lambda_{\text{max}} = 22$. 24 points in $\theta$ from Gauss–Legendre quadrature were used to project out the potential expansion coefficients.

Sufficient number of partial waves necessary for convergence of the cross sections were used; in the higher collision energy region the maximum value of $J$ employed was 360. The CS approximation was adopted for collision energies greater than $10.5933$ cm$^{-1}$.

Table 1: Rotational Excitation Energies (cm$^{-1}$) of HCl for the Ground Vibrational State$^a$

| $j$ | $E_j$ | $E_j$ |
|-----|-------|-------|
| 0   | 0.00000 | 14 | 2201.22000 | 28 | 8252.30728 |
| 1   | 21.18448 | 15 | 2511.86400 | 29 | 8815.01400 |
| 2   | 63.54072 | 16 | 2842.16008 | 30 | 9393.37200 |
| 3   | 127.04328 | 17 | 3191.92722 | 31 | 9986.99968 |
| 4   | 211.65400 | 18 | 3560.91768 | 32 | 10595.50272 |
| 5   | 317.32200 | 19 | 3948.92200 | 33 | 11218.47408 |
| 6   | 443.98368 | 20 | 4355.69400 | 34 | 11855.49400 |
| 7   | 591.56272 | 21 | 4780.79728 | 35 | 12506.13000 |
| 8   | 759.97008 | 22 | 5224.51072 | 36 | 13169.93688 |
| 9   | 949.10400 | 23 | 5686.08488 | 37 | 13846.45672 |
| 10  | 1158.85000 | 24 | 6165.18000 | 38 | 14535.21888 |
| 11  | 1389.08088 | 25 | 6661.72000 | 39 | 15235.74000 |
| 12  | 1639.65400 | 26 | 7173.31048 | 40 | 15947.52400 |
| 13  | 1910.42488 | 27 | 7705.62072 | 41 | 16668.30400 |

Note. $^a$ $E_j = B_0 j (j + 1) - D_0 j^2 (j + 1)^2$, where $B_0$ and $D_0$ are the rotational constant and the centrifugal distortion constant of HCl, respectively.

3. RESULTS AND DISCUSSION

3.1. State-to-state and Total Deexcitation Cross Sections

State-to-state quenching cross sections were computed for initial HCl rotational levels of $j = 1, 2, \ldots, 20$. Rotational energy levels are presented in Table 1 for the basis set adopted in the current calculation, which were obtained using rotational constant $B_0 = 10.5933$ cm$^{-1}$ (Irikura 2007) and centrifugal distortion constant $D_0 = 0.00053$ cm$^{-1}$ (Rank et al. 1965).

As examples, the state-to-state quenching cross sections from initial levels $j = 5$ and 15 are presented in Figures 1(a) and (b), respectively. Cross sections using the CS approximation begin at 2000 cm$^{-1}$ and are seen to be in excellent agreement with those obtained with the CC method.

The cross sections display resonances in the intermediate energy region from $\sim 0.1$ cm$^{-1}$ to $\sim 10$ cm$^{-1}$ due to quasibound levels supported by the attractive part of the interaction potential. The $|\Delta j| = |j' - j| = 1$ transition dominates the quenching for all $j$ (shown here for $j = 5$ and $j = 15$), with the cross sections generally increasing with increasing $j'$ with that for $j' = 0$ being the smallest.

The total deexcitation cross section from an initial state $j$ can be obtained by summing over all final states $j'$. Figure 2 displays the total deexcitation cross section for quenching from selected initial levels $j = 2, 4, 6, \ldots, 18$, and 20. Generally, the total quenching cross sections have similar behavior, but differences result for small $j$ at high energy due to a limited number of final exit channels. Each of the cross sections exhibits the behavior predicted by Wigner (1948) threshold laws at ultralow collision energies below $\sim 10^{-4}$ cm$^{-1}$, where only $s$-wave scattering contributes and the cross sections vary inversely with the relative velocity. Except for $j = 2$ the total deexcitation cross sections decrease to a global minimum near 500 cm$^{-1}$.

1 All state-to-state deexcitation cross sections and rate coefficients are available on the UGA Molecular Opacity Project Web site (http://www.phy.sast.uga.edu/ugamop/). The rate coefficients are also available in the BASECOL (Dubernet et al. 2006) and the Leiden Atomic and Molecular Database (LAMDA; Schöier et al. 2005) formats.
3.2. State-to-state Deexcitation Rate Coefficients

The state-to-state thermal rate coefficients can be calculated by thermally averaging the appropriate state-to-state cross sections over a Maxwell–Boltzmann distribution of kinetic energy $E_j$. To our knowledge, there has been no published experimental rate coefficients available for rotational transitions of HCl by collisions with He. Therefore, we compare our rate coefficients with the theoretical results of Neufeld & Green (1994), Lanza & Lique (2012), and Ajili et al. (2013), which were obtained over a limited temperature range of 10 to 300 K. As examples, Figures 3 and 4 show selected transitions for state-to-state deexcitation rate coefficients from initial HCl levels $j = 1, 3,$ and $7$. Generally, our results show very good agreement with that of Lanza & Lique (2012) and Ajili et al. (2013), which were computed using different potentials.

For initial state $j = 1$, Figure 3(a) shows that the present rate coefficients are larger than those of Neufeld & Green (1994), Lanza & Lique (2012), and Ajili et al. (2013) in the temperature range from 10 to 300 K, but their rate coefficients approach our results with increasing temperature. Figure 3(b), which displays state-to-state deexcitation rate coefficients from initial level $j = 3$, shows that the results of Neufeld & Green (1994), Lanza & Lique (2012), and Ajili et al. (2013) agree well with the present rate coefficients, except that for quenching to $j' = 0$ the rate coefficients of both Neufeld & Green (1994) and Lanza & Lique (2012) are larger than the present results.

State-to-state rate coefficients from initial state $j = 7$ are given in Figure 4 where comparison of the present results with the rate coefficients of Lanza & Lique (2012) show excellent agreement. Except for the transition $j = 5 \rightarrow j' = 3$, the rate coefficients of Neufeld & Green (1994) generally show good agreement with present results. These differences are likely related to differences in the adopted PESs (see below). For illustration, in Figure 5 we also present the state-to-state deexcitation rate coefficients for temperatures from 0.1 K to 3000 K for initial levels $j = 10$ and 20. Over the whole temperature range considered, the rate coefficients generally increase with increasing temperature for all transitions. Further,
Figure 3. State-to-state rotational deexcitation rate coefficients from initial states \( j = 1 \) and 3 of HCl due to collisions with He. (a) \( j = 1 \), (b) \( j = 3 \). Lines: present results; filled symbols: Neufeld & Green (1994); open symbols: Lanza & Lique (2012); dotted line with cross symbols: Ajili et al. (2013).

Figure 4. Same as Figure 3, but for initial state \( j = 7 \).

One can clearly see that the rate coefficients decrease with increasing \( |\Delta j| = |j' - j| \) with the \( \Delta j = -1 \) transitions dominant.

4. UNCERTAINTY IN SCATTERING CALCULATIONS

One essential prerequisite for accurate cross section and rate coefficient calculations is the availability of a PES with high accuracy. However, the quality of the PES depends not only on the methods used for the interaction energy calculation, but also the accuracy and reliability of the potential fitting and extension to long range. Convergence testing was performed in our calculations by using sufficiently large basis sets and adjustment of other calculation parameters. Consequently, the uncertainty associated with our cross section calculation is related primarily to the uncertainty in the adopted PES. In this
work, the SAPT PES of Murdachaew et al. (2004) was applied. As discussed by Murdachaew et al. (2004) the main features of the HCl–He PES are a minimum in the linear configuration He–H–Cl, global minimum at the He–Cl–H configuration, and a saddle point close to the T-shaped configuration. This also applies to PESs of Fajin & Fernandez (2006) and Lanza & Lique (2012). However, the major difference between the three potentials is the well depth of the global minimum. To estimate the uncertainty of the cross sections and rate coefficients calculated from the PES of Murdachaew et al. (2004), a simple approach is to scale the SAPT PES by the largest and smallest ratio of the well depths of the three PESs. Of course, the cross section and rate coefficients depend on the detailed structure of the potential including the shape, well depth, and position of the minimum which relies heavily on the methods applied in the HCl–He potential calculation. Here, the well depth is used to illustrate the uncertainty in scattering calculations. We calculated the deexcitation cross section and rate coefficient for the $j = 1 \rightarrow j’ = 0$ transition using the SAPT PES scaled by factors of 1.0322 and 0.9688, respectively, i.e., a variation of $\pm 3\%$.

In Figure 6 we compare the $j = 1 \rightarrow j’ = 0$ quenching cross sections and rate coefficients obtained using the scaled SAPT potential with the results obtained from the original SAPT potential. Due to differences in the PES well depths, it can be seen that the cross sections and rate coefficients show evident disagreement at low collision energy and low temperature, $T \leqslant 20$ K. In the van der Waals interaction-dominated regime, the rate coefficients exhibit an oscillatory temperature dependence due to the presence of resonances. The magnitudes, widths, and positions of the resonances are sensitive to the details of the PES. However, for high collision energy and

Figure 5. State-to-state rotational deexcitation rate coefficients from initial state $j = 10$ and $j = 20$ of HCl due to collisions with He atoms as a function of temperature. (a) $j = 10$, (b) $j = 20$. (A color version of this figure is available in the online journal.)

Figure 6. Rotational deexcitation (a) cross section and (b) rate coefficient for $j = 1 \rightarrow j’ = 0$ using the SAPT potential and scaled SAPT potentials. Solid line: SAPT potential of Murdachaew et al. (2004), dashed line: scaled SAPT potential with factor of 1.0322, dotted line: scaled SAPT potential with factor of 0.9688. (A color version of this figure is available in the online journal.)
high temperature, the cross sections and rate coefficients from the scaled and original SAPT PES generally converge. In other words, the uncertainty due to the accuracy of the SAPT PES is negligible at high temperatures. We estimate the uncertainty in the computed rate coefficients to be 12%, 4%, and 1.3% at 1, 10, and 100 K, respectively.

5. ASTROPHYSICAL APPLICATIONS

Rate coefficients for collisional excitation and deexcitation are of importance in describing the dynamics of energy transfer processes in interstellar objects. In particular, accurate rotational and vibrational excitation rates are needed to interpret microwave and infrared observations of the interstellar gas for non-LTE line formation. Further, the thermal balance of interstellar gas is partly determined by cooling processes involving molecular collisional excitation followed by radiative decay. Despite some progress in laboratory measurements of state-to-state collisional rate coefficients and cross sections, astrophysical models depend almost exclusively on theoretical data. Experiments do provide, when available, some confidence in the theoretical rate coefficients.

As discussed in the Introduction, HCl has been observed in emission and absorption in a variety of astronomical environments. Agúndez et al. (2011) reported observations of the \( j = 1 \rightarrow 0, 2 \rightarrow 1, \) and 3–2 rotational lines of H\(^{35}\)Cl and H\(^{37}\)Cl in the carbon star envelope IRC+10216 using the Herschel/HIFI instrument. It was inferred that HCl is produced in the inner layers of the envelope close to the asymptotic giant branch star. Recently, by observing the H\(^{37}\)Cl and H\(^{35}\)Cl 1–0 transitions with the HIFI spectrometer, Codella et al. (2012) presented the first detection of HCl toward protostellar shocks. It is expected that more highly excited rotational lines may be observed with SOFIA in the future. However, except for the set of calculations done for temperatures between 10 and 300 K and \( j < 7 \) by Neufeld & Green (1994), Lanza & Lique (2012), and Ajili et al. (2013), no other computations of the He excitation rate coefficients have appeared. Therefore, the current rate coefficient calculations, which extend from 0.1 to 3000 K, are the most comprehensive to date for He and can be utilized in a variety of applications augmenting the datasets developed for He, H\(_2\), and electrons (see also the LAMDA Web site; Schönbr et al. 2005).

The rate coefficients for molecular scattering with para-H\(_2\) are often estimated using available rate coefficients with He by the application of a constant reduced-mass scaling factor of 1.4 (Schöier et al. 2005). However, Lique et al. (2008) calculated the rate coefficients for SiS scattering with para-H\(_2\) and compared their results to the SiS–He rate coefficients (Vincent et al. 2007) scaled by the H\(_2\)/He reduced-mass factor and found significant differences. In much earlier work, Schaefer (1990) found large deviations at temperatures of 100 K and below when comparing directly calculated rotational excitation rate coefficients for HD due to H\(_2\) and those obtained by reduced mass scaling of HD–He rates. Applying such a procedure to the current HCl–He rates coefficients to estimate rate coefficients for H\(_2\) is therefore not recommended.

The hyperfine structure splitting of HCl occurs due to its non-zero nuclear spin. Though hyperfine transitions are not considered here, the hyperfine excitation cross sections can be estimated from the current results using an infinite-order sudden approximation approach (Lanza & Lique 2012; Faure & Lique 2012).

6. CONCLUSION

Cross sections and rate coefficients for rotational quenching of HCl due to He collisions have been studied using the CC method and the CS approximation on the PES of Murdachaew et al. (2004) for excited initial rotational levels of HCl up to \( j = 20 \). State-to-state rate coefficients are obtained over a wide temperature range from 0.1 to 3000 K and available in tables formatted for astrophysical applications. The very good agreement with the results of Lanza & Lique (2012) and Ajili et al. (2013), computed on different PESs confirms the accuracy of the present calculations of the rate coefficients. The uncertainty in the current rate coefficient calculation, deduced by scaling the adopted potential, is less than 4% at temperatures of astrophysical interest, comparable to the divergence in the well depth of recently available PESs.

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