Spin-orbit quenching of the $\text{C}^+(2\,P)$ ion by collisions with para- and ortho-$\text{H}_2$

François Lique,$^{1, a}$ Ghofran Werfelli,$^{2, 3}$ Philippe Halvick,$^2$ Thierry Stoecklin,$^2$
Alexandre Faure,$^4$ Laurent Wiesenfeld,$^4$ and Paul J. Dagdigian$^5$

$^1$LOMC - UMR 6294, CNRS-Université du Havre, 25, Rue Philippe Lebon, BP 540, 76058 Le Havre, France
$^2$Institut des Sciences Moléculaires, Université de Bordeaux, CNRS UMR 5255, 33405 Talence Cedex, France
$^3$Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis, Campus Universitaire, Tunis 2092, Tunisia
$^4$UJF-Grenoble 1/CNRS-INSU, Institut de Planétologie et d’Astrophysique de Grenoble (IPAG), UMR 5274, Grenoble F-38041, France
$^5$Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218-2685, USA

(Received 6 April 2013; accepted 7 May 2013; published online 30 May 2013)

Spin-orbit (de-)excitation of $\text{C}^+(2\,P)$ by collisions with $\text{H}_2$, a key process for astrochemistry, is investigated. Quantum-mechanical calculations of collisions between $\text{C}^+$ ions and para- and ortho-$\text{H}_2$ have been performed in order to determine the cross section for the $\text{C}^+(2\,P_{3/2} \rightarrow 2\,P_{1/2})$ fine-structure transition at low and intermediate energies. The calculation are based on new $\textit{ab initio}$ potential energy surfaces obtained using the multireference configuration interaction method. Corresponding rate coefficients were obtained for temperatures ranging from 5 to 500 K. These rate coefficients are compared to previous estimations, and their impact is assessed through radiative transfer computation. They are found to increase the flux of the $2\,P_{3/2} \rightarrow 2\,P_{1/2}$ line at 158 $\mu$m by up to 30% for typical diffuse interstellar cloud conditions. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4807311]

I. INTRODUCTION

Carbon, having an ionization potential of 11.26 eV, is the most abundant element in the Interstellar Medium (ISM) with an ionization potential less than 13.6 eV. Hence, the $\text{C}^+(2\,P_{3/2} \rightarrow 2\,P_{1/2})$ transition of singly ionized carbon is globally the dominant cooling line in the general diffuse ISM.$^1$ In addition, the $\text{C}^+$ ion is a sensitive tracer of density and temperature in diffuse clouds and in photon dominated regions (PDRs), and the $\text{C}^+$ line provides an important probe of the gas content and star formation processes in the Milky Way and other galaxies. In fact, the $\text{C}^+$ fine-structure transition is the galaxy’s strongest emission line. Recently, high spectral resolution observations of $\text{C}^+$ became available with the Herschel Space Observatory,$^{2, 3}$ providing the astronomical community with a powerful tool to probe the diffuse ISM and PDRs.

In the ISM, excitation to the $2\,P_{3/2}$ level of $\text{C}^+$ is due to inelastic collisions with either neutral hydrogen atoms, molecules, or electrons. Hence, it is crucial to determine accurate temperature variation of the spin-orbit (de-)excitation of $\text{C}^+$ due to collisions with $\text{H}, \text{H}_2$, and $\text{e}^-$ in order to interpret incisively the $\text{C}^+$ emission observed using new high resolution telescopes.

$\text{C}^+$ and $\text{H}_2$ collisions can lead to the formation of the $\text{CH}^+$ cation. This reaction has been extensively studied both theoretically and experimentally (see Ref. 4 and references therein). However, the reaction is endothermic by 3211 cm$^{-1}$, and at typical interstellar temperatures, for $\text{H}_2$ in its ground vibrational state, the reaction does not occur. The only process that takes place is the $\text{C}^+(2\,P_{1/2}) + \text{H}_2(v, j) \rightarrow \text{C}^+(2\,P_{3/2}) + \text{H}_2(v', j')$ (de-)excitation process.

This process was already studied by several authors. Chu and Dalgarno$^5$ first argued that collinear collisions ($C_{\infty v}$ symmetry) are the most probable in the excitation of the fine-structure transition and performed a calculation for the collinear $\text{C}^+-\text{H}–\text{H}$ collision, in which the hydrogen molecule was treated as a spherical atom. Similarly, Toshima$^6$ estimated the cross section by analogy with the $\text{C}^+-\text{He}$ interaction.

The first realistic study was performed by Flower and Launay.$^{2, 8}$ They performed calculations of the spin orbit excitation cross sections of $\text{C}^+$ in collisions with both para- and ortho-$\text{H}_2$. They obtained the angular dependence of the long-range potential expansion from the standard perturbation theory and derived the same expansion at short range, from available potential energy curves (PECs)$^9$ in linear and perpendicular approaches. This elegant approach was used later on for studying similar cationic systems, for example, $\text{Ne}^+(2\,P) + \text{H}_2$.$^{10}$

Because of the potentially important role of this process in astrochemistry, the present study revisits the fine structure excitation of $\text{C}^+$ in collisions with para- and ortho-$\text{H}_2$, using new potential energy surfaces (PESs) computed from highly correlated $\textit{ab initio}$ methods.

The paper is organized as follows. Section II describes the PESs used in this work. Section III contains a brief description of the scattering calculations. In Secs. IV and V, we present and discuss our results.

---

1)Electronic mail: francois.lique@univ-lehavre.fr
II. POTENTIAL ENERGY SURFACE

As mentioned in the Introduction, the C\(^+\) + H\(_2\) reaction has been the object of extensive theoretical modeling and several ground state CH\(_3\) PESs are available.\(^{11-13}\) However, these PESs cannot be used for the fine-structure collisional excitation of C\(^+\) by H\(_2\) since the latter process implies non Born-Oppenheimer terms that were not computed in the C\(^+\) + H\(_2\) reaction studies.

Here, we focus on low-temperature collision rate coefficients so that vibrational excitation of H\(_2\), as well as chemical reaction, do not occur. The H\(_2\) molecule may thus be considered to be rigid. As shown previously,\(^{14}\) properly averaged molecular geometries provide a better description than equilibrium geometries. Accordingly, we used the H\(_2\) bond length \(r = 1.44874\) bohr (Ref. 15).

We consider the C\(^+\) ion as a frozen C\(^2+\) core plus a 2\(\rho\) valence electron. Adopting the body fixed coordinate system, the C\(^+\)-H\(_2\) interaction energy may be expanded in terms of spherical harmonic functions such as\(^7\)

\[
V(R, \tilde{r}, \tilde{\rho}) = 4\pi \sum_{\lambda_1, \lambda_2, \lambda, \mu} v_{\lambda_1, \lambda_2, \lambda, \mu}(R)[Y_{\lambda_1-\mu}(\tilde{r})Y_{\lambda,\mu}(\tilde{\rho})],
\]

where \(Y\) denotes a spherical harmonic, \(\tilde{r}\) the orientation of the H\(_2\) internuclear axis, \(\tilde{\rho}\) the position of the active electron relative to the atomic nucleus, and \(R\) the separation of the C\(^+\) ion and the centre of mass of the H\(_2\) molecule. The index \(\lambda_1\) is even because H\(_2\) is homonuclear, and \(\lambda_2 = 0\) and 2 since the unpaired electron is in a \(p\) orbital.\(^{16, 17}\)

Calculation of global PESs for such an interacting system is a complex task as can be seen in Ref. 18. However, the problem can be simplified by using the following approach. For collisions at low temperature, the probability of rotational excitation of H\(_2\) is low, and previous studies have shown that terms with \(\lambda_1 > 2\) are small so we truncated the \(\lambda_1\) series to \(\lambda_1 \leq 2\). Flower and Launay\(^7\) have thus shown that the corresponding expansion can be obtained from a limited number of H\(_2\) orientations. Three distinct electronic configurations are available to the 2\(\rho\) valence electron. This gives three different PESs, which correlate to the \(2\Sigma_1\), \(2\Pi_1\), and \(2\Pi_2\) states in C\(_{2v}\) symmetry, and to the \(2\Sigma^+\) and \(2\Pi\) states in C\(_{\infty v}\) symmetry. Then, the five radial coefficients \(v_{000}, v_{202}, v_{220},\) and \(v_{222}\) of the potential expansion in Eq. (1) may be derived from the five C\(_{2v}\) and C\(_{\infty v}\) PECs, significantly reducing the complexity of the problem.

The C\(^+\)-H\(_2\) interaction energy has been computed with the multireference configuration interaction method with the Davidson correction (MRCI+Q). The molecular orbitals were obtained from a complete active space self-consistent field (CASSCF) calculation in which 5 electrons are distributed in 6 active orbitals, using the aug-cc-pVQZ basis set.\(^9\) In these calculations, all valence molecular orbitals and all valence electrons were taken as active. Between 38 and 49 points were calculated for each of the five different PECs, the largest intermonomer separation being \(R = 40\) bohr. In order to calculate reliable long-range interaction energies, the thresholds for the neglect of one- and two-electron integrals were lowered to \(10^{-13}\), and the CASSCF and MRCI convergence thresholds were tightened to \(10^{-9}\). Ab initio calculations were performed with the MOLPRO package.\(^{20}\)

The ab initio energies were interpolated with the one-dimensional Reproducing Kernel Hilbert Space method (RKHS).\(^{21}\) We used the reciprocal power reproducing kernel with \(m = 2\), which extrapolates outside ab initio points with \(R^{-3}\) and \(R^{-4}\) long range asymptotics.\(^{12}\)

The \(R\)-dependence of the C\(_{2v}\) and C\(_{\infty v}\) C\(^+\)-H\(_2\) PECs is displayed in Fig. 1. For the three surfaces, the interaction energy is more attractive in C\(_{2v}\) symmetry than in C\(_{\infty v}\) symmetry. The two lowest PECs (\(2\Pi\), or \(2\Pi_1\) and \(2\Pi_2\)) show significant potential energy wells (9097 cm\(^{-1}\) for the \(2\Pi_2\) state), while the third PEC (\(2\Sigma^+\) or \(2\Sigma_1\)) is hardly attractive. In C\(_{\infty v}\) symmetry, energy barriers (not visible in Fig. 1) of 22.8 cm\(^{-1}\) and 24.4 cm\(^{-1}\) can be observed in the long-range interaction at \(R = 11.0\) bohr and \(R = 10.7\) bohr for the \(2\Sigma^+\) and \(2\Pi\) states, respectively. These energy barriers arise from the charge-quadrupole interaction:

\[
U(R, \theta) = \frac{Q\Theta}{R^3} P_2(\cos \theta),
\]

where \(Q\) is the charge of the carbon atom, \(\Theta = 0.46\) a.u. is the quadrupole moment of H\(_2\), and \(\theta\) is the angle between \(\tilde{r}\) and \(\tilde{R}\). This is the longest range interaction between C\(^+\) and H\(_2\), and it is repulsive in C\(_{\infty v}\) symmetry but attractive in C\(_{2v}\).

![FIG. 1. Ab initio potential energy curves for C\(^+\)-H\(_2\) interaction. (a) \(2\Sigma\) and \(2\Pi\) (C\(_{\infty v}\) symmetry) potential energy curves as a function of \(R\). (b) \(2\Sigma_1\), \(2\Pi_1\), and \(2\Pi_2\) (C\(_{2v}\) symmetry) potential energy curves as a function of \(R\).](image-url)
symmetry. This interaction dominates at very long range. However, when \( R \) decreases, it is the attractive contributions in electrostatic, induction, and dispersion energies (which scale as \( R^{-n} \) with \( n \geq 4 \)), which, in turn, become dominant.

While the global shapes of the PECs presented in Fig. 1 are similar to those calculated by Flower and Launay,\(^8\) there are important differences in the depths of the potential energy wells, which are almost two times larger, owing to the high-level calculation of the electronic correlation energy performed in the present work. The equilibrium bond lengths are also significantly shorter in our PECs, by about 1 bohr for the \( ^2\Pi, ^2\Sigma_1, \) and \( ^2\Sigma_2 \) PECs, and by about 3 bohr for the \( ^2\Sigma_1 \) PEC.

From the five selected orientations of the \( \text{C}^+ - \text{H}_2 \) interaction, we have obtained the five radial coefficients \( v_{000}, v_{200}, v_{020}, v_{220}, \) and \( v_{222} \) in the body-fixed frame. The dependence of these coefficients on \( R \) is shown in Fig. 2.

As one can see, the coefficients that directly imply both \( \text{C}^+ \) and \( \text{H}_2 \) transitions (i.e., \( \lambda_1 = \lambda_2 = 2 \)) are relatively small in magnitude. Hence, we could anticipate that cross sections for simultaneous excitation of \( \text{C}^+ \) and \( \text{H}_2 \) will be small compared to others. These coefficients were then transformed into space fixed frame coefficients in order to perform scattering calculations.\(^17\)

### III. SCATTERING CALCULATIONS

In a full description of the collision including the electronic fine-structure of the \( \text{C}^+ \) ion, the states in the \( \text{C}^+ + \text{H}_2 \) arrangement are described by the quantum numbers \( j (j = 0, 1, 2), \) the rotational quantum number of \( \text{H}_2, \) and \( j_\sigma (j_\sigma = 1/2 \) or \( 3/2 \)), the total electronic angular momentum of the \( \text{C}^+ \) ion. The calculation of the integral cross section for the collision of an open-shell atomic species such as \( \text{C}^+(j_\sigma) \) with \( \text{H}_2(j) \) to give \( \text{C}^+(j'_\sigma) + \text{H}_2(j') \) is given in Ref. 17.

All the scattering calculations were performed with the HIBRIDON package.\(^22\) In all the calculations, the propagation was performed from 1 to 80 bohr. The energy levels were computed with the following experimental \( \text{C}^+ \) and \( \text{H}_2 \) spectroscopic parameters: the rotational constant of \( \text{H}_2 \) was \( B_0 = 59.3340 \) cm\(^{-1} \) (Ref. 23) and the spin-orbit constant of \( \text{C}^+ \) was \( A_{\text{SO}} = 42.28 \) cm\(^{-1} \).\(^24\) The \( \text{C}^+ - \text{H}_2 \) collision reduced mass is \( \mu = 1.726 \) amu. At each collision energy, the maximum value of the total angular momentum \( J_{\text{max}} \) was set large enough that the inelastic cross sections were converged to within 0.01\( \) \AA\(^2\). For example, at a total energy of 2800 cm\(^{-1} \), \( J_{\text{max}} = 100. \)

The \( \text{H}_2 \) rotational basis included all states with \( j \leq 12 \). This large number of rotational levels was imposed by the large well depth of the PESs, leading to an important coupling with closed rotational channels for low/intermediate energy collisions. Indeed, at short range, potential energy becomes available for temporary rotational excitation during the collision.

Cross sections were calculated on a grid of 1360 total energies over the range \( 1 \leq E_{\text{tot}} \leq 2800 \) cm\(^{-1} \). From the inelastic cross sections \( \sigma_{\text{gt}}(E_c) \), one can obtain the corresponding thermal rate coefficients at temperature \( T \) by an averaging over the collision energy \( (E_c) \):

\[
k_{i \rightarrow f}(T) = \left( \frac{8}{\pi \mu (k_B T)^2} \right)^{1/2} \times \int_0^\infty \sigma_{i \rightarrow f}(E_c) E_c \exp(-E_c/k_B T) dE_c, \tag{3}\]

where \( k_B \) is the Boltzmann constant, and \( i \) and \( f \) denote the initial and final levels of the colliders, respectively. Calculations of the cross sections at total energies up to 2800 cm\(^{-1} \) allow the determination of rates up to 500 K without loss of accuracy.

As will be shown in Sec. IV, the energy-dependent cross sections exhibit numerous resonance features, and a detailed investigation of these resonances would require a very fine energy grid. However, because of the averaging over collision energy [Eq. (3)], these narrow resonances will have little effect on the relaxation rate coefficients. Thus, we made a compromise and we used a step size of 1 below 1000 and 5 from 1000 to 2800 (energies given in cm\(^{-1} \)).

### IV. RESULTS

Using the computational scheme described above, we determined the energy variation of the \( \text{C}^+ - \text{H}_2(j = 0, 1, 2) \) spin-orbit relaxation cross sections. The possible (de-)excitation of \( \text{H}_2 \) has been taken into account. Figure 3 illustrates the energy dependence of the collisional de-excitation cross sections obtained from the present calculations for spin orbit quenching of \( \text{C}^+ \) by \( \text{H}_2(j = 0, 1) \).

The de-excitation cross sections are nearly monotonically decreasing functions of the collision energy. Many resonances are found over all the collisional energies explored. These are a consequence of the quasibound states arising from tunneling through the centrifugal energy barrier (shape resonances), or from the presence of an attractive potential well that allows \( \text{H}_2 \) to be temporarily trapped into the well, hence leading to the formation of quasibound states (Feshbach resonances) before the complex dissociates.\(^25\)

One can also see that there are differences between the collisions of \( \text{C}^+ \) with the two nuclear spin modifications of \( \text{H}_2 \). The cross section for collisions with \( \text{H}_2(j = 1) \) is slightly larger than that with \( \text{H}_2(j = 0) \). This trend was already observed for molecules such as CO (Ref. 26) and SiS (Ref. 27).
and can be explained by the important anisotropy of the PESs versus the H₂ angular coordinate. The energy-dependent de-excitation cross section for C⁺ spin-orbit relaxation in collision with ortho-H₂ (j = 1) appears to have a smoother energy dependence than the cross section for collision with para-H₂ (j = 0). This is a result of the fact that there are many more, and hence overlapping, resonances for ortho-H₂ than for para-H₂. Hence, the resonance features are mostly washed out for ortho-H₂.

We used these calculated energy-dependent cross sections to obtain excitation and de-excitation rate coefficients for the electronic relaxation of spin-orbit excited C⁺ ions in collisions with H₂(j = 0–2) by carrying out a Boltzmann average over the collision energy [see Eq. (3)]. We present in Fig. 4 the temperature variation of these state-to-state rate coefficients. This complete set of (de-)excitation rate coefficients is available online from the LAMDA²⁸ and BASECOL²⁹ websites.

One can observe a relatively weak variation of the rate coefficients with increasing temperature. It is also apparent from Fig. 4 that the rate coefficient for the simultaneous de-excitation of C⁺ and H₂(j = 2) is smaller than that of C⁺ de-excitation alone; however, the rate coefficient for simultaneous de-excitation is not negligible. Generally, the rate coefficients for collisions with H₂(j > 0) are similar. In the present case, however, the rate coefficient for collision with H₂(j = 2) is smaller than that for collision with H₂(j = 1). This may be explained by the magnitude of simultaneous C⁺ and H₂(j = 2) de-excitation rate coefficients. Indeed, for collisions between C⁺(2P3/2) and H₂(j = 2), de-excitation of both C⁺ and H₂ can occur. This leads to a smaller magnitude of the rate coefficient for the pure spin orbit quenching process, contrary to collisions between C⁺(2P3/2) and H₂(j = 1) where only the spin orbit quenching process can occur. However, if we consider the total quenching of C⁺(2P3/2) in collisions with H₂(j = 2) [i.e., the sum of the rotationally elastic H₂(j = 2) → H₂(j = 2) transition and the rotationally inelastic H₂(j = 2) → H₂(j = 0) transition], we find that the relaxation rate coefficients of C⁺(2P3/2) by H₂(j = 1) and H₂(j = 2) are similar.

The same behavior can also explain the temperature dependence of the C⁺(2P3/2) + H₂(j = 0) → C⁺(2P3/2) + H₂(j = 0) rate coefficients. Indeed, at intermediate temperature, the excitation of H₂(j = 0) → H₂(j = 2) occurs and can compete with the rotationally elastic process H₂(j = 0) → H₂(j = 0), hence leading to a small decrease in the latter rate coefficient at higher temperature.

We compare in Table I the spin orbit quenching rate coefficients of C⁺ by H₂ determined in the present work with those obtained by Flower and Launay.⁸ As one can see, there is a reasonable agreement between the present rate

---

**TABLE I.** Comparison of C⁺ 2P3/2 → 2P3/2 spin orbit quenching rate coefficients (units: 10⁻¹⁰ cm³ s⁻¹).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>H₂(j = 0) → H₂(j = 0)</th>
<th>H₂(j = 1) → H₂(j = 1)</th>
<th>H₂(j = 2) → H₂(j = 2)</th>
<th>H₂(j = 2) → H₂(j = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>This work 4.36</td>
<td>This work 5.29</td>
<td>This work 4.43</td>
<td>This work 0.73</td>
</tr>
<tr>
<td>20</td>
<td>FL77²⁸ 3.00</td>
<td>FL77²⁸ 5.33</td>
<td>FL77²⁸ 4.40</td>
<td>FL77²⁸ 0.73</td>
</tr>
<tr>
<td>50</td>
<td>4.53</td>
<td>4.30</td>
<td>4.37</td>
<td>4.58</td>
</tr>
<tr>
<td>100</td>
<td>4.67</td>
<td>4.30</td>
<td>5.45</td>
<td>4.72</td>
</tr>
<tr>
<td>200</td>
<td>4.59</td>
<td>4.60</td>
<td>5.62</td>
<td>4.99</td>
</tr>
<tr>
<td>300</td>
<td>4.48</td>
<td>...</td>
<td>5.71</td>
<td>5.20</td>
</tr>
<tr>
<td>500</td>
<td>4.36</td>
<td>...</td>
<td>5.79</td>
<td>5.43</td>
</tr>
</tbody>
</table>

⁸Flowers and Launay (Ref. 8).
coefficients and those computed by Flower and Launay.\(^8\)
However, the present rate coefficients are larger, by 30%–50%, than those of Flower and Launay, which are currently used in astrophysical applications. The largest deviations occur at low temperature \((T < 100 \text{ K})\). The difference can be simply explained by the use of different PESs (see Sec. II). Indeed, Flower and Launay\(^8\) used PESs with an inaccurate short-range part and stated that their rate coefficients may present inaccuracies up to 50% for temperature greater than 50 K, and probably even more at lower temperatures. However, one can note that despite significant differences in the position and magnitude of the potential well, the overall agreement is reasonable between the two sets of calculations. This comparison shows that spin orbit quenching process is not highly sensitive to the accuracy of the PESs. The present work thus should provide reasonably accurate calculations of the \(C^+\) spin-orbit relaxation rate coefficients for collisions with \(H_2\).

It is interesting to note that the temperature variation of the \(C^+(2P_{3/2}) + H_2(j = 0) \rightarrow C^+(2P_{1/2}) + H_2(j = 0)\) rate coefficient of Flower and Launay\(^8\) is not the same as in the present study. Their rate coefficient increases with increasing temperature, whereas the present rate coefficient for this process increases and then decreases with increasing temperature. This can certainly be explained by the small magnitude of their rate coefficient for simultaneous excitation of \(C^+\) and \(H_2\), which is less competitive with the \(C^+(2P_{3/2}) + H_2(j = 0) \rightarrow C^+(2P_{1/2}) + H_2(j = 0)\) process than in the present results. This effect may be a signature of the different PESs used.

V. DISCUSSION AND CONCLUSION

We have presented quantum mechanical calculations of rate coefficients for the spin-orbit relaxation of \(C^+(2P_{3/2})\) ion by \(H_2\) molecules in both the \textit{para} and \textit{ortho} nuclear spin modifications. The calculations are performed using new PESs obtained from highly correlated \textit{ab initio} calculations. The spin-orbit quenching of \(C^+(2P_{3/2})\) is more efficient when the \(H_2\) molecule is in the \(j = 1\) rotational level rather than in \(j = 0\). The quenching is less efficient, but not negligible, for simultaneous \(C^+\) and \(H_2(j = 2)\) (de-)excitation. The new rate coefficients will significantly help in interpreting \(C^+\) emission observed with current and future telescopes.

As a first and preliminary application and in order to test the impact of the new rate coefficients on the \(C^+ + 2P_{3/2} \rightarrow 2P_{1/2}\) emission line, we have performed radiative transfer calculations for the physical conditions typical of diffuse interstellar clouds, where hydrogen is mostly molecular. We note that the state-to-state rate coefficients for \(H_2\) initially in \(j = 0\) and \(j = 2\) were summed over the final \(j\) states \((j' = 0, 2)\) and averaged over a thermal (Boltzmann) initial rotational state distribution. \textit{Ortho-}\(H_2\) was restricted to \(j = 1\). The \textit{ortho} to \textit{para} ratio of \(H_2\) is \(\sim 1\) in the diffuse ISM\(^30\) and this value was adopted in the following. Non-local thermodynamic equilibrium (non-LTE) calculations were performed with the RADEX code\(^31\) using the Large Velocity Gradient (LVG) approximation for an expanding sphere. The \(H_2\) density, \(C^+\) column density, and line width were taken from typical values derived by Langer et al.\(^2\) towards the “dark” \(H_2\) component of diffuse interstellar clouds, namely, \(n(H_2) = 300 \text{ cm}^{-3}\), \(N(C^+) = 2 \times 10^{17} \text{cm}^{-2}\), and \(\Delta v = 3 \text{ km s}^{-1}\). The temperature was varied from 10 to 250 K. Results are presented in Fig. 5. It can be observed that the line flux of the \(2P_{3/2} \rightarrow 2P_{1/2}\) transition increases rapidly above \(\sim 25 \text{ K}\), showing that \(C^+\) emission is indeed a probe of “warm” diffuse gas. The present rate coefficients are also found to produce a similar but larger line flux than those of Flower and Launay.\(^8\) The difference is actually the largest below 50 K, where it can reach 30%, as expected from the comparison in Table I.

ACKNOWLEDGMENTS

This work has been supported by the Agence Nationale de la Recherche (ANR-HYDRIDES), Contract No. ANR-12-BS50-0011-01, and by the CNRS national program “Physique et Chimie du Milieu Interstellaire.”

29BASECOL, Ro-vibrational Collisional Database, see http://basecol.obspm.fr/.