

Rotational excitation of interstellar molecular ions by electrons

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Abstract.

Electrons are known to be efficient in rotationally exciting molecular ions in cold ionized media. Rotational effects have also been shown to affect the dissociative recombination (DR) process. Electron collisions are thus expected to play a significant role in the thermalization and dissociation dynamics of molecular ions, both in the laboratory and in space. Using the molecular **R**-matrix method combined with the Adiabatic-Nuclei-Rotation (ANR) approximation corrected for threshold and closed-channel effects, we have computed new rate coefficients for the rotational excitation of H_3^+ and HCO^+ by electrons at temperatures from 10 to 1 000K. At temperatures above rotational thresholds, rotational rates are found to compete or even dominate those of dissociative recombination, suggesting that electron collisions provide a possible source of rotational (de)excitation in DR measurements.

1. Introduction

Since the discovery of CH^+ in space 70 years ago [1], more than a dozen of positive molecular ions have been detected in the interstellar medium. Among these, H_3^+ and HCO^+ and their deuterated isotopologues are particularly important in the context of interstellar gas-phase chemistry [2]. Along with CH^+ , H_3^+ and HCO^+ have also been detected in diffuse clouds where the fractional ionization is high ($n(e)/n(\text{H}) \sim 10^{-4}$). In such environments, electrons play a very important role in the destruction (through DR) and in the thermalization (through inelastic collisions) of positively charged species. Moreover, these two processes are closely related because rotational effects can significantly affect the DR process, as shown for example in the case of H_2^+ [3, 4] or H_3^+ [5, 6]. These experimental and theoretical studies indeed suggest that rotational effects can increase or decrease the DR rate coefficients by factors up to ~ 3 . Thus, the most recent calculations on H_3^+ [6] have shown that an improved agreement with the experimental DR measurements can be obtained by assuming rotational temperatures significantly larger than those derived in the experiments, suggesting the possibility that the ions get rotationally 'hot' before the DR rate is measured. Interestingly, in the case of diatomic ions, a theoretical study has shown that rotation plays a role mainly for the indirect DR process and for light

molecules [7]. It is therefore not clear whether rotational effects are significant in the case of heavy polyatomic ions like HCO^+ , even if the indirect mechanism is dominant [8].

In the astrophysical context, the sensitivity of the DR process to the rotational temperature of the ions is particularly important because the rotational populations of interstellar molecules are generally not at thermal equilibrium. The accurate determination of the ion abundances therefore requires rotationally resolved rate coefficients for both inelastic collisions and DR. This is particularly important for H_3^+ whose simple chemistry has been used to infer the primary cosmic-ray ionization rate in the diffuse interstellar medium [9]. It is to be noted, in this context, that the rotational dependence of the H_3^+ DR rate is ignored in current astrochemistry studies (e.g. [10, 11]). In the present paper, we discuss the competitive role of rotational and dissociation dynamics at low energy for the two astrophysically relevant ions H_3^+ and HCO^+ . The objective is to illustrate the relative rate of rotational (de)excitation and DR for a non-polar and a highly polar ion. Section 2 briefly describes the theoretical approach employed to compute the rotational rate coefficients. Illustrative results are presented in Section 3 while conclusions are drawn in Section 4.

2. Theory of rotational excitation

The reference method for obtaining electron-impact excitation rates has been the Coulomb-Born (CB) approximation [12, 13]. This approach assumes that the collisional excitation rates are determined by long-range interactions. A standard further approximation is to consider only the dominant long-range term. Within this model, the CB theory predicts that only single jumps in rotational quanta ($\Delta J = 1$) are allowed for polar species. Recent **R**-matrix calculations combined with the adiabatic-nuclei-rotation (ANR) approximation have been applied to several molecular ions and have shown that the inclusion of short-range interactions actually lead to significant rates for transitions with $\Delta J > 1$, and particularly $\Delta J = 2$ [14]. On the other hand, the collisional propensity rules were generally found to be consistent with the CB theory. As a result, dipole-allowed transitions are always preferred for highly polar ions like HCO^+ and the K quantum number is essentially conserved for symmetric-top molecules like H_3^+ [15].

These **R**-matrix studies were, however, hampered by the use of the ANR approximation which is expected to become invalid close to a rotational threshold [16]. Thus, the previous **R**-matrix calculations applied the “kinematic correction” factor k'/k , where k (k') is the initial (final) momentum of the electron, designed for neutral targets (see [17] and references therein). Very recently, we have shown in the case of H_3^+ that this correction is in fact incorrect for molecular ions [18]. Thus, by comparison with rovibrational quantum defect theory (QDT) calculations based on the treatment described in [19], pure ANR excitation cross sections have been shown to be accurate for kinetic energies above the resonance regime caused by rotational closed-channels. These resonances were found to occur for transitions with $\Delta J = 1$ and $\Delta K = 0$ and for these, an analytical formula for averaging transition probabilities over the resonance structure was formulated. In the case of transitions with $\Delta J > 1$, the ANR theory was shown to be accurate down to threshold, provided a simple “Heaviside correction” is applied to the excitation cross sections. Full details can be found in [18]. The corrected H_3^+ rotational cross sections were thus shown to be large and finite at threshold, in accord with the Wigner law for an attractive Coulomb field, with a significant but moderate contribution from closed channels. The range of validity of the adiabatic theory is therefore much wider than the usual classically derived condition that the impacting electron energy be large compared to the threshold energy.

These results contrast with the case of neutral non-polar targets such as H_2 for which rotational cross sections fall steeply near threshold (e.g. [17]). This fundamental difference between ions and neutrals, which was actually predicted sometime ago (although the role of closed-channels was not considered) [20], reflects the influence of the strong Coulomb field which ensures that the time scale for electron motion is always rapid compared to the nuclear motion.

At the same time, the Coulomb potential provides the energy to access closed channels, thus creating substantial resonance effects. As such, H_3^+ is actually quite an unfavorable system for the ANR theory owing to its large rotational spacings that make threshold and closed-channel effects important up to large kinetic energies (> 10 meV). In the case of HCO^+ , however, resonances due to the transitions $\Delta J > 1$ are not expected to contribute significantly to the dipolar rate coefficients owing to the large HCO^+ dipole (3.9 D) and its small rotational spacings. As a result, the Heaviside correction has been applied to the ANR excitation cross sections of HCO^+ but closed-channel effects were ignored. These latter will be investigated in detail in a future work.

Finally, it should be noted that the rotational rate coefficients presented below are different from those previously published [14, 21] since the threshold behaviour of the cross sections has been reconsidered and corrected. The differences are however generally modest except at low temperatures ($T < 300$ K). These new rates will be published elsewhere soon.

3. Results

Examples of rotational (de)excitation rate coefficients for H_3^+ are presented in Fig. 1 along with the experimental DR rate [22]. The rotational temperature of H_3^+ in the CRYRING experiment was estimated to be $\sim 20\text{--}60$ K, indicating that the only levels with significant population are the para (1, 1) and ortho (1, 0) levels. It can be noticed in Fig. 1 that the rotational excitation rates peak at relatively high temperatures, well above 100 K, as a consequence of the large rotational excitation energies of H_3^+ (e.g. 250 K for $(1, 1) \rightarrow (2, 1)$). Thus, rotational excitation rates are orders of magnitude lower than the DR rates below 100 K. On the other hand, rotational deexcitation and DR rates have comparable magnitude down to 10 K. This suggests that rotational cooling by electrons is an important mechanism in low temperature DR experiments while rotational heating is expected to occur only at larger temperature. Such effects have indeed been observed in recent long-time storage-ring experiments at the TSR facility in Heidelberg [5, 23]. A proper model of these measurements, i.e. the time dependence of the DR rate as a function of cooling time, clearly requires the inclusion of accurate state-to-state rotational rates.

Fig. 1 shows also the rotational (de)excitation rate coefficients for the same transitions, $(1, 1) \leftrightarrow (2, 1)$ calculated using the scattering matrix obtained in the QDT approach. Details of the approach can be found elsewhere (see for example, Refs. [18, 19]). In this treatment, only p -wave states of the incident electron are accounted for. The s -wave does not contribute into the final rate of rotational (de)excitation, because J is conserved for the s -wave scattering. Waves with $l > 1$ do not contribute significantly because H_3^+ is a relatively compact ion: the scattering phase shifts in $l > 1$ waves are much smaller than in the p -wave. These considerations are in agreement with the results obtained with ANR method: since p -wave $\text{H}_3^+ + e^-$ collisions have the largest scattering amplitude, the rate coefficients of rotational (de)excitation are the largest for $\Delta J = 1, 2$. Examples of rotational transitions with high rate coefficients are $(1, 1) \leftrightarrow (2, 1) \leftrightarrow (3, 1)$; $(1, 1) \leftrightarrow (3, 1)$; $(1, 0) \leftrightarrow (3, 0)$. The energy-dependent cross-sections for this type of transitions have many Rydberg resonances, which belong to excited rovibrational states of the ion (see for example, Fig. 2 of Ref. [18]). The Rydberg states associated with the rotational state, which is closed for ionization, can play a significant role in rotational (de)excitation. Thermal rates do not have any resonant structure because the Rydberg resonances are smeared out by the Maxwell-Boltzmann distribution. However, the presence of the resonances in the rotational (de)excitation spectrum increases the average thermal rate (see Fig. 3 of Ref. [18]). The difference between the two theoretical results (ANR and QDT) in Fig. 1 is mainly due to these Rydberg states, which are accurately included in the QDT approach but only approximatively in ANR (through an analytical averaging [18]). Nevertheless, the agreement between the two approaches is good.

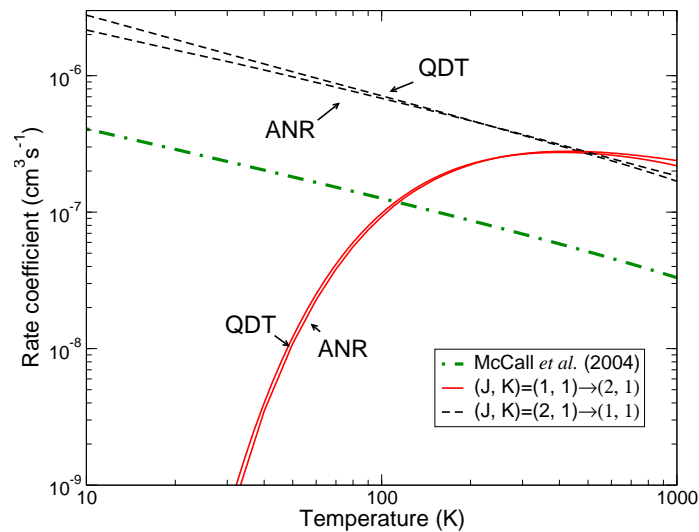


Figure 1. Rate coefficients as a function of temperature for electron- H_3^+ collisions. The solid and dashed lines denote typical rotational transitions for para- H_3^+ , calculated using two different methods: ANR and QDT. The dash-dotted line gives the power law fit of the experimental DR rate, obtained from CRYRING ion storage-ring measurements [22].

Examples of rotational (de)excitation rate coefficients for HCO^+ are presented in Fig. 2 along with the experimental DR rate [24]. It is striking to note that the DR rate is comparable to that of H_3^+ (i.e. about $10^{-7} \text{ cm}^3\text{s}^{-1}$ at 100 K) while the rotational rates are much larger, by typically two orders of magnitude. This reflects the large electron-dipole interaction which, for dipoles larger than about 2 D, completely dominate the dipolar transitions [14]. Furthermore, owing to the small HCO^+ rotational spacings (e.g. 4 K for $0 \rightarrow 1$), excitation rates for the low lying transitions do not decrease at the lowest temperatures investigated here (e.g. the $0 \rightarrow 1$ rate coefficient is still above $10^{-5} \text{ cm}^3\text{s}^{-1}$ at 10 K). This suggests that both a significant rotational cooling and rotational heating by electron collisions is expected in low temperature DR measurements in HCO^+ . It is, however, not clear yet whether these rotational effects will significantly affect the dissociation dynamics.

4. Conclusions

The competitive role of electron-impact rotational (de)excitation and dissociative recombination at low energy has been discussed and illustrated in the case of two astrophysically relevant ions: H_3^+ and HCO^+ . Electron collisions have been shown to provide a possible source of rotational (de)excitation in DR measurements, in particular for polar and heavy ions like HCO^+ . In low density astrophysical media, these collisions can also contribute to the thermalization of the ions. In this context, it should be noted that the TSR storage-ring experiments have shown that H_3^+ gets trapped in long-lived rotational states [25], an effect that is beginning to be observed astrophysically [26]. Under these circumstances electron collisions could be particularly important for determining actual (nonthermal) rotational distributions [27]. We finally note the recent suggestion to use rotational emission of HCO^+ caused by electron-impact to probe electron densities in interstellar C-type shocks [28].

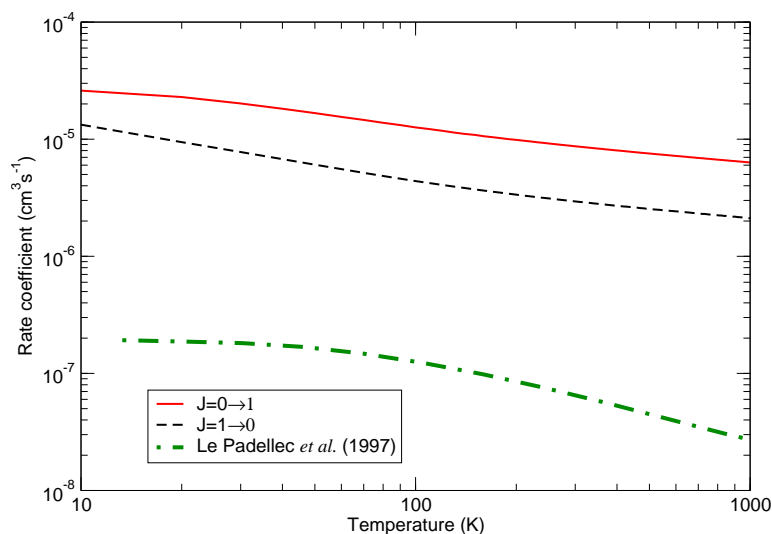


Figure 2. Rate coefficients as a function of temperature for electron–HCO⁺ collisions. The solid and dashed lines denote typical rotational transitions calculated using the ANR theory. The dash-dotted line gives the experimental DR rate obtained from the experimental cross sections of Le Padellec *et al.* (1997) [24].

Acknowledgments

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