

OPEN ACCESS

## Dissociative recombination of $\text{HCO}^+$

To cite this article: Åsa Larson *et al* 2005 *J. Phys.: Conf. Ser.* **4** 148

View the [article online](#) for updates and enhancements.

### You may also like

- [Role of Ni Addition in Corrosion Behavior of Model Interface Between Rust Layer and Steel Matrix on Weathering Steels](#)  
Yu Sugawara, Waka Inoue, Ayaka Yomogida et al.
- [Voltammetry Combined with on-Line HPLC for the Electro-Oxidation of Formamidine Disulfide](#)  
Wei Zhang
- [Preparation and Characterization of Electroless Deposited Fe-Ni Alloy Films](#)  
Takayo Yamamoto, Tomio Nagayama, Yoshiki Konno et al.



**ECS** The Electrochemical Society  
Advancing solid state & electrochemical science & technology

### 242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Early hotel & registration pricing ends September 12

Presenting more than 2,400 technical abstracts in 50 symposia

The meeting for industry & researchers in

**BATTERIES**  
**ENERGY TECHNOLOGY**  
**SENSORS AND MORE!**

 Register now!

  **ECS Plenary Lecture featuring M. Stanley Whittingham,**  
Binghamton University  
Nobel Laureate –  
2019 Nobel Prize in Chemistry



# Dissociative recombination of $\text{HCO}^+$

Åsa Larson,<sup>1</sup> Stefano Tonzani,<sup>2</sup> Robin Santra<sup>3,4</sup> and Chris H Greene<sup>3</sup>

<sup>1</sup> Dept. of Physics, Royal Institute of Technology, Stockholm, Sweden

<sup>2</sup> Dept. of Chemistry and JILA, University of Colorado, Boulder, CO 80309-0440 USA

<sup>3</sup> Dept. of Physics and JILA, University of Colorado, Boulder, CO 80309-0440 USA

E-mail: aasa@physics.kth.se

**Abstract.** We report on *ab initio* calculations relevant for dissociative recombination of  $\text{HCO}^+$ . From accurate quantum chemistry calculations, it is found that the electron collision is driven by capture into Rydberg states. The Renner-Teller effect is not important for higher Rydberg states. From calculated potentials, the effective quantum numbers are fitted in three dimensions. The model of the electron collision is simplified using an adiabatic approximation, where one of the Jacobi coordinates is treated adiabatically. Then the electron collision is described using two different theoretical methods. Preliminary results on autoionization widths for Rydberg states and dissociative recombination cross section are given.

## 1. Introduction

The  $\text{HCO}^+$  molecular ion is one of the key ions in the chemistry of interstellar clouds. The major destruction channel of this ion is believed to be dissociative recombination (DR) by low-energy electrons. Therefore it has been a crucial task to study electron collisions with  $\text{HCO}^+$  ions. Numerous experimental studies have been carried out on this reaction using different techniques, such as stationary afterglows [1,2], flowing afterglows [3–5], a merged beam study [6] and, very recently, a storage ring experiment [7]. The thermal rate coefficient at 300 K is found in several studies to be about  $2.0 \cdot 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  [5], and its temperature dependence is stronger than the  $T^{-0.5}$  dependence usually found when DR is driven by the direct mechanism where an excited neutral diabatic state is crossing the ionic ground state close to its minimum. Therefore it has been proposed that there is no direct mechanism for DR of  $\text{HCO}^+$  and instead the process is driven by electron capture into ro-vibrationally excited Rydberg states [1]. The DR cross section has been measured in the two ion-beam experiments [6,7]. The cross section of Le Padellec *et al.* is overall up to an order of magnitude larger than the one measured by Geppert *et al.* Absorption measurements [4], and recently the storage ring experiment [7], have shown a complete dominance of dissociation into H + CO. Also relevant in this context is the series of publications on autoionization of  $\text{HCO}$  Rydberg states carried out by Grant *et al.* [8].

The DR mechanism of  $\text{HCO}^+$  is controversial. There are two previous theoretical studies of this reaction. Kraemer and Hazi [9] carried out Complete Active Space SCF (CASSCF) calculations at linear geometry on the ground state of  $\text{HCO}^+$  and some of the excited states of  $\text{HCO}$  relevant for DR. No indications were found of a neutral state crossing the ionic ground state near the minimum. However, in the studies by Talbi *et al.* [10] carried out at linear geometry, a direct mechanism for DR of  $\text{HCO}^+$  was proposed on the basis of Multi-Reference Configuration Interaction (MRCI) calculations with localized

<sup>4</sup> Present address: Institute for Theoretical Atomic, Molecular and Optical Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, USA

orbitals. Using a diabaticization procedure, the adiabatic potential curves generated a repulsive neutral state crossing the ionic ground state near the minimum. Bates [11] has expressed skepticism about this diabaticization procedure, calling the DR of  $\text{HCO}^+$  an “enigma” and proposing instead a “multi-step mechanism” for DR of  $\text{HCO}^+$ , where the electron capture and dissociation proceed through a series of  $\Delta v = 1$  transitions between Rydberg states of HCO.

One of the main goals of this study is to establish the reaction mechanism. To do this, accurate quantum chemistry calculations of both valence and Rydberg states of HCO have been performed. The Renner-Teller effect is strong in the ground ( $\tilde{X}^2A'$ ) and first excited ( $\tilde{A}^2A''$ ) states of HCO [12], so we need to assess its importance for the electron capture and predissociation in DR, as the similar Jahn-Teller effect was found to be crucial in DR of  $\text{H}_3^+$  [13].

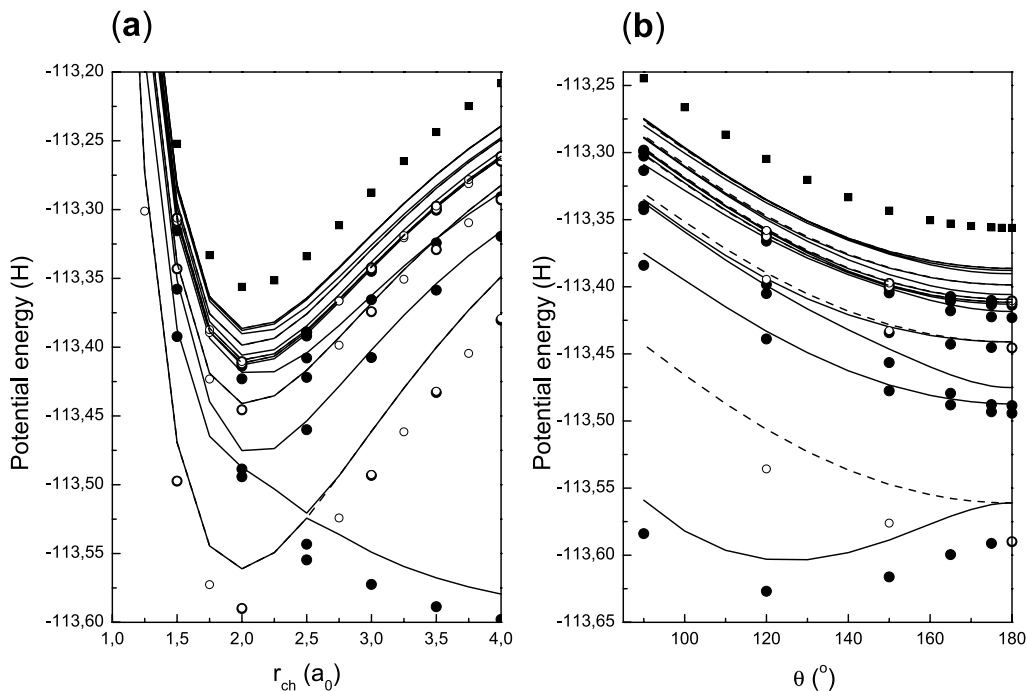
In the next section we will describe the quantum chemistry calculations we carried out. This is followed by a description of the theoretical treatment of the electron collision. Then the DR reaction is studied using two different theoretical methods. To test our model, calculated autoionization widths of HCO Rydberg states are compared with experimental results.

## 2. Quantum chemistry calculations

The quantum chemistry calculations are carried out using the MOLPRO program package [14]. In order to accurately describe the HCO Rydberg states, diffuse basis functions have to be manually added to the Dunning correlation-consistent triple zeta basis set, aug-cc-pVTZ [15]. This has to be done carefully in order to obtain convergence of relevant molecular orbitals and avoid linear dependence problems. We add seven s-functions, seven p-functions and three d-functions at the H-atom and at the midpoint between the C and O atoms. The exponent for each new s- and p-Gaussian is decreased by a factor 2.5 relatively to the previous one. For the d-functions a factor 3 is used. In order to have an accurate treatment of both valence and Rydberg states we performed MRCI calculations. To simplify our task, we took advantage of Koopman’s theorem, according to which the electron affinity can be approximated by the energy of a virtual molecular orbital of a single determinant Hartree-Fock (HF) wave function. This approximation is not very accurate for a neutral system, however, for a cation, it is (as we will show) surprisingly good. By starting with a HF calculation on the ion, we know that we will have a good orbital description for the Rydberg states and we will not need many configurations in the MRCI expansion to describe the Rydberg states. We calculated the potential energy surfaces in the three dimensional space where  $1.0 a_0 \leq r_{\text{CH}} \leq 4.0 a_0$ ,  $1.78 a_0 \leq r_{\text{CO}} \leq 2.55 a_0$  and  $180^\circ \geq \theta \geq 90^\circ$ . We used 4000 reference configurations and 1.2 million single and double excitations. The calculated MRCI potentials are displayed in figure 1 together with the potentials we obtain when we approximate the potential of a Rydberg state with the MRCI energy of the ion plus the molecular orbital energy according to Koopmans’ theorem. As can be seen from the figure, the two methods give energies that follow each other closely. There is a dissociative state that interacts with the  $n = 2$  Rydberg states, but there is no interaction with the higher Rydberg states, so after diabaticization of the surfaces, this state cannot cross the ionic ground state close to its minimum. Therefore the DR has to take place via an indirect mechanism through the Rydberg states.

At linear geometry, the lowest state of HCO is the doubly degenerate  $^2\Pi(2p\pi)$  state. As soon as the molecule is bent, the potentials of the two states split up into the Renner-Teller components  $A'$  and  $A''$  [12]. The ground  $\tilde{X}^2A'$  state has a minimum around  $\theta = 125^\circ$ . However, since only the high Rydberg states are important for electron capture, we have to study the Renner-Teller effect in the high Rydberg states in order to conclude whether it is important for DR or not. Between the  $n = 2$  and  $n = 3$   $p\pi$  Rydberg states though, the Renner-Teller splitting decreases much more than the  $n^{-3}$  scaling usually assumed for Rydberg states. We therefore conclude that the Renner-Teller effect is not important for the electron capture.

The adiabatic quantum defect  $\mu_{l\lambda}$  is related to the energy difference between the potential of the ion ( $V_{\text{ion}}$ ) and neutral Rydberg state ( $V_{nl\lambda}$ ) according to Mulliken’s equation  $V_{nl\lambda} = V_{\text{ion}} - 1/(2(n - \mu_{l\lambda})^2)$ , where  $\nu_{nl\lambda} = n - \mu_{l\lambda}$  is the effective quantum number. In the MQDT formalism the quantum defects



**Figure 1.** Potential energy of the ground state of the  $\text{HCO}^+$  ion and energies of several excited states of the neutral HCO molecule calculated (a) at linear geometry ( $\theta = 180^\circ$ ) and  $r_{\text{CO}} = 2.0877 a_0$  and (b) as functions of the bending angle, where  $r_{\text{CH}} = 2.0 a_0$  and  $r_{\text{CO}} = 2.0877 a_0$  are fixed. Black squares show the potential of the ion, calculated using MRCI. The filled symbols indicated the MRCI potentials of excited states of HCO with  $A'$  symmetry, while the open symbols are states of  $A''$  symmetry. The corresponding potentials obtained using Koopmans' theorem as described in the text are shown with full and dashed lines.

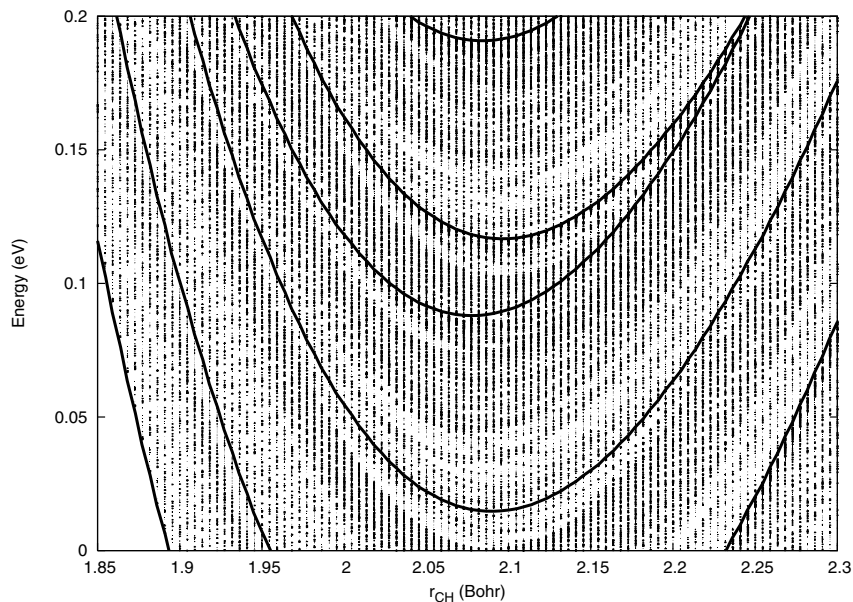
below the ionization threshold are smoothly connected to scattering phase shifts above threshold. We use a diabatic representation of the quantum defects to fit the  $3s\sigma$ ,  $3d\sigma$ ,  $3p\sigma$ ,  $3p\pi_x$  and  $3p\pi_y$  Rydberg states. For the  $\sigma$  states, we include off-diagonal couplings that had a Gaussian shape in the  $r_{\text{CH}}$  distance, with a fixed width and position, but variable magnitude. For the diagonal elements, we assume a polynomial form, including up to cubic terms for the  $r_{\text{CH}}$  dependence. The fitted parameters are then splined over  $r_{\text{CO}}$  and  $\theta$ . The fit was carried out for the  $n = 3$  Rydberg states and in order to check it we compare the fitted states with higher and lower Rydberg states. For the  $n = 2$  states, the fit is not satisfactory. We do not reproduce the large Renner-Teller splitting observed for the lowest  $\Pi$  states. Also we have a bad description of the repulsive valence state that diabatically goes up at the inner wall of the ionic ground state. However, the quantum defects for the higher ( $n = 4$ ) Rydberg states are well reproduced.

### 3. Electron scattering

To describe the electron collision, in the present study we neglect rotational motion and we include the vibrational motion using the so-called vibrational frame transformation.

#### 3.1. Adiabatic approximation

We simplify our description of the vibrational motion using the adiabatic approximation. To improve the adiabaticity of the curves we use Jacobi coordinates that mimic closely the normal modes. The  $R = r_{\text{CH}}$  coordinate is defined as the distance between the H and C atoms, while the  $r$  coordinate is the distance from the center of mass of C-H to the O atom and  $\vartheta$  is the angle between  $R$  and  $r$ . In the adiabatic approximation, the ionic vibrational wave functions are calculated by first solving the Schrödinger



**Figure 2.** Calculated  $\text{HCO}^+$   $R$ -dependent vibrational eigenvalues (lines) and HCO resonances (dots).

equation for the  $r$  and  $\vartheta$  coordinates, keeping  $R$  as a variable parameter. The dependence on the  $R$  parameter is then included in a later stage of the calculation as described below. The difference between vibrational energies calculated using this procedure and doing a direct three dimensional diagonalization is about  $10 \text{ cm}^{-1}$  for the lower ( $02^00$ ,  $001$ ) vibrational modes, but for higher energies the difference increases to a few hundreds of  $\text{cm}^{-1}$ .

### 3.2. MQDT formalism

From the *ab initio* calculated quantum defects, the corresponding clamped nuclei S-matrix is obtained. In the MQDT framework, the vibrational motion is included using a vibrational frame transformation and in the adiabatic approximation we carry out the transformation for the  $(r, \vartheta)$  coordinates first, calculating the  $R$ -dependent S-matrix

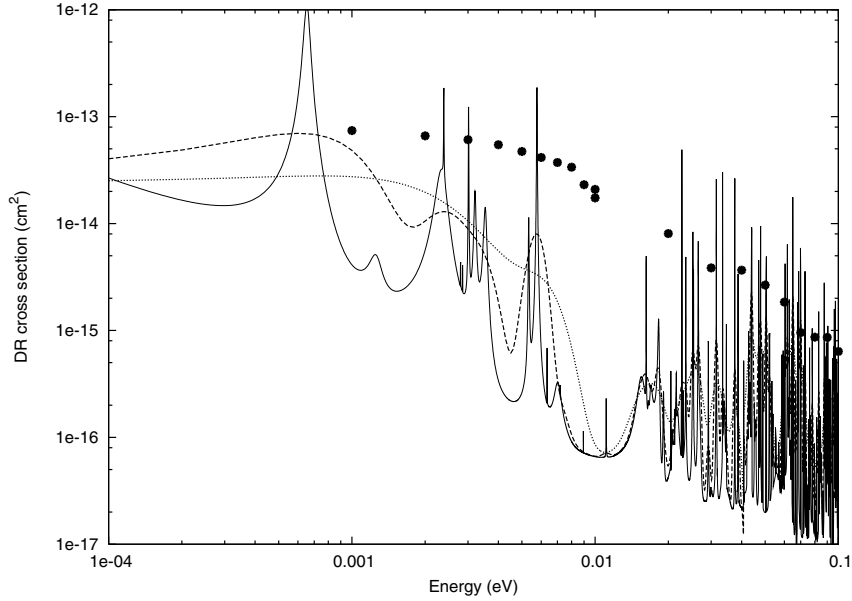
$$S_{\Lambda v_r v_\vartheta, \Lambda' v'_r v'_\vartheta}(R) = \left\langle \left\langle \phi_{v_r v_\vartheta} | S_{\Lambda, \Lambda'} | \phi_{v'_r v'_\vartheta} \right\rangle \right\rangle, \quad (1)$$

where  $\phi_{v_r v_\vartheta}$  is the vibrational wave function of the  $\text{HCO}^+$  ion calculated at fixed  $R$  and  $\Lambda = l, \lambda$  is the electronic index. In the equation above, the double brackets refer to integration over the  $(r, \vartheta)$  coordinates.

The positions and widths of the resonances are calculated by time-delay analysis as described elsewhere [16]. Thousands of resonances are obtained (shown in figure 2), corresponding to interactions with Rydberg states in different  $(v_r v_\vartheta)$  vibrational levels. All resonances are relatively narrow with autoionization widths  $\Gamma_i(R) < 1 \text{ cm}^{-1}$ . The curves are the vibrational eigenvalues of the ion.

### 3.3. O'Malley approach

One way to calculate the DR cross section is by applying methods developed for diatomic molecules. O'Malley [17] derived a formula for calculating the DR cross section when a repulsive neutral state is crossing the ionic ground state close to the minimum. From figure 2 we conclude that in the present case we have a manifold of resonances and most of them are not repulsive. We therefore have to modify the



**Figure 3.** Calculated (—) and measured (●) [6] cross sections for DR of  $\text{HCO}^+$ . To compare with the measured cross section, the calculated cross section has been convoluted with a 1 meV (·····) and 3 meV (- - -) Gaussian energy distribution.

O'Malley formula to capture into nuclear bound resonances

$$\sigma(E) = \frac{\pi^2}{E} \sum_{k, \nu_R} |\langle X_{\nu_R}^k | \Gamma_k | X_0^{\text{ion}} \rangle|^2 e^{-\rho(E)}, \quad (2)$$

where  $X_{\nu_R}^k(R)$  and  $X_0^{\text{ion}}(R)$  are the vibrational wave functions of the resonance and ion and  $\rho(E)$  is included to account for loss due to autoionization. We are presently working on the calculation of the vibrational wave functions needed to apply formula (2).

### 3.4. Siegert states

It should be noted that the calculated cross section is overall smaller than the cross section measured by Le Padellec *et al*, especially for  $E \geq 0.01$  eV where the theoretical cross section drops several orders of magnitude. Another approach is to use Siegert (outgoing-wave) boundary conditions [18] in the C-H degree of freedom. This allows the description of outgoing flux in predissociation. The next step is to use the Siegert states ( $\phi_{\nu_R}$ ) to calculate the full S-matrix

$$S_{\Lambda \nu_r \nu_\vartheta \nu_R, \Lambda' \nu_r' \nu_\vartheta' \nu_R'} = \langle \phi_{\nu_R} | S_{\Lambda \nu_r \nu_\vartheta, \Lambda' \nu_r' \nu_\vartheta'} | \phi_{\nu_R'} \rangle. \quad (3)$$

Then the channel elimination is applied to obtain the physical S-matrix ( $S_{i,i'}^{\text{phys}}$ ) of dimension  $N_o \times N_o$  where  $N_o$  is the number of open channels [16]. When the Siegert states are used, the physical S-matrix will not be unitary and the difference from unitarity will be related to the DR cross section

$$\sigma(E_{\text{el}}) = \frac{\pi}{2E} \left( 1 - \sum_{i'=1}^{N_o} S_{i,i'}^{\text{phys}}(E) S_{i',i}^{\dagger \text{phys}}(E) \right), \quad E_{\text{el}} = E - E_i, \quad (4)$$

where  $E_i$  is the initial state of the ion. The results are converged when we include 40 adiabatic states and 9 C-H Siegert states for each adiabatic potential. To converge these states, we need about 40 grid points in  $r$  and  $\vartheta$  and 100 points for  $R$ . The resulting DR cross section is shown in figure 3.

**Table 1.** Calculated energies and widths of the autoionizing HCO resonances. Here  $n$  is the approximate principal quantum number and  $(v_{CH}, v_{\theta}, v_{CO})$  is the ionic vibrational mode of the resonance.  $\Gamma_{\text{box}}$  is the width calculated using box-states, while  $\Gamma_{\text{Siebert}}$  is calculated using Siebert states. The widths measured by Grant *et al* [8] are displayed as  $\Gamma_{\text{exp}}$ .

Energy (H)	$n$	$(v_{CH}, v_{\theta}, v_{CO})$	$\Gamma_{\text{box}}$ ( $\text{cm}^{-1}$ )	$\Gamma_{\text{Siebert}}$ ( $\text{cm}^{-1}$ )	$\Gamma_{\text{exp}}$ ( $\text{cm}^{-1}$ )
$8.65 \cdot 10^{-5}$	6	(1,0,0)	1	3	-
$3.13 \cdot 10^{-3}$	7	(1,0,0)	3	6	-
$2.12 \cdot 10^{-4}$	7	(0,0,1)	0.08	2	10
$2.30 \cdot 10^{-3}$	8	(0,0,1)	0.026	1	8
$6.50 \cdot 10^{-3}$	12	(1,0,0)	0.018	0.7	2.5
$2.30 \cdot 10^{-4}$	12	(0,1,0)	0.013	0.6	1.5
$7.53 \cdot 10^{-4}$	13	(0,1,0)	0.012	0.45	1.25

### 3.5. Autoionization widths

To test the wave functions and quantum defects used in the present study we compare calculated autoionization widths with the measurements of Grant *et al.* using high resolution double-resonance spectroscopy. The vibrational wave functions for the C-H stretch are either box states or the Siebert states described above. The resulting widths are displayed in table 1. As can be seen, the measured widths are up to an order of magnitude larger than the calculated widths.

## 4. Results and discussion

From our extensive MRCI calculations there is no indication of a diabatic state crossing the ionic ground state close to its minimum. Instead the repulsive valence state is dominated by a singly excited configuration and it is only crossing some of the lower Rydberg states. Therefore the rate-determining step for DR in  $\text{HCO}^+$  is capture into Rydberg states.

There is a large Renner-Teller splitting in the lowest  $^2\Pi$  state, but for the higher  $^2\Pi$  Rydberg states, the Renner-Teller effect is found to be negligible.

The calculated DR cross section is relatively small compared with the measured cross section by Le Padellec *et al.* [6]. The calculated values for autoionization widths are also smaller than the experimental results. Several limitations of the present theoretical model might help explain the discrepancies. First, the adiabatic approximation might break down and we are presently working on including non-adiabatic effects between the adiabatic resonances. It should be noted that the autoionization widths increase by about an order of magnitude when Siebert states are used instead of box-states. This is an indication that predissociation is important. However, the most repulsive state (the valence  $2p\sigma$  state) is not accurately described by the quantum defects included in the present model. Also, from other theoretical studies it is known that at higher energies a doubly excited neutral state will cross the ionic potential and interact with the Rydberg states at larger distances. This state is not included in the model and this might explain the drop of the calculated cross section compared with experiment for  $E \geq 0.01$  eV. In order to implement these states, energy-dependent quantum defects have to be used. To summarize, this is one of the first studies of dissociative recombination of a polyatomic ion that includes all vibrational degrees of freedom quantum mechanically. It is a challenging project with many questions unanswered. However, we do believe we have established the mechanism for DR of  $\text{HCO}^+$ .

## Acknowledgments

This work has been supported in part by the Department of Energy, Office of Science, NERSC supercomputing resources and the Keck Foundation through computational resources. Å Larson is

supported by the Knut and Alice Wallenberg Foundation and by The Swedish Foundation of International Cooperation in Research and Higher Education (STINT). We thank V Kokoouline for discussions and advice.

## References

- [1] Leu M T, Biondi M A and Johnsen R 1973 *Phys. Rev. A* **8** 420
- [2] Ganguli B, Biondi M A, Johnsen R and Dulaney J L 1988 *Phys. Rev. A* **37** 2543
- [3] Adams N G, Smith D and Alge E 1984 *J. Chem. Phys.* **81** 1778  
Adams N G and Smith D 1985 *Molecular Astrophysics. State of Art and Future Directions. Proceedings of the NATO Advanced Research Workshop* p 657  
Adams N G and Babcock L M 1994 *Astrophys J.* **434** 184  
Rowe B R, Gomet J C, Canosa A, Rebrion C and Mitchell J B A 1992 *J. Chem. Phys.* **96** 1105  
Gougousi T, Golde M F and Johnsen R 1997 *Chem. Phys. Lett.* **265** 399
- [4] Adams N G, Herd C R, Geoghegan M, Smith D, Canosa A, Gomet J C, Rowe B R, Queffelec J L and Morlais M 1991 *J. Chem. Phys.* **94** 4852
- [5] Laubé S, Le Padellec A, Sidko O, Rebrion-Rowe C, Mitchell J B A and Rowe B R 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2111
- [6] Le Padellec A, Sheehan C, Talbi D and Mitchell J B A 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 319
- [7] Geppert W D *et al.* To be published
- [8] Mayer E E and Grant E R 1995 *J. Chem. Phys.* **103** 10513  
Mayer E E, Hedderich H G and Grant E R 1997 *J. Chem. Phys.* **108** 1886  
Mayer E E, Hedderich H G and Grant E R 1998 *J. Chem. Phys.* **108** 8429  
Robinson J D, Foltynowicz R J and Grant E R 2000 *J. Chem. Phys.* **112** 1701  
Zückerman E J, Mayer E E, Foltynowicz R J, Robinson J D, Hui Jen S, Konopka M C, Sanford T, Hedderich H G, Chen I-C and Grant E R 2000 *J. Chem. Phys.* **113** 5372
- [9] Kraemer W P and Hazi A U 1985 *Molecular Astrophysics. State of Art and Future Directions. Proceedings of the NATO Advanced Research Workshop* p 575  
Kraemer W P and Hazi AU 1989 *Dissociative Recombination: Theory, Experiment and Applications* (Singapore: World Scientific) p 62
- [10] Talbi D, Pauzat F and Ellinger Y 1988 *Chem. Phys.* **126** 291  
Talbi D, Hickman A P, Pauzat F, Ellinger Y and Berthier G 1989 *Astrophys J.* **339** 231
- [11] Bates D R 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 5479
- [12] Goldfield E M, Gray S K and Harding L B 1993 *J. Chem. Phys.* **99** 5812  
Loettgers A, Untch A, Keller H-M, Schinke R, Werner H-J, Bauer C, and Rosmus P 1997 *J. Chem. Phys.* **106** 3186
- [13] Kokoouline V, Greene C H and Esry B D 2001 *Nature* **412** 891  
Kokoouline V and Greene C H 2003 *Phys. Rev. A* **68** 012703
- [14] MOLPRO, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, M. Schütz and others, <http://www.molpro.net>, Birmingham, UK, 2003
- [15] Dunning T H Jr. 1989 *J. Chem. Phys.* **90**, 1007
- [16] Aymar M, Greene C H and Luc-Koenig E 1996 *Rev. Mod. Phys.* **68** 1015
- [17] O'Malley T F 1966 *Phys. Rev.* **150** 14
- [18] Tolstikhin O I, Ostrovsky V N and Nakamura H 1997 *Phys. Rev. Lett.* **79** 2026  
Tolstikhin O I, Ostrovsky V N and Nakamura H 1998 *Phys. Rev. A* **58** 2077