Dissociative recombination of HCO$^+$

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Abstract. We report on ab initio calculations relevant for dissociative recombination of 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 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 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 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 HCO Rydberg states carried out by Grant$^+$ et al. [8].

The DR mechanism of 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 HCO$^+$ and some of the excited states of 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 HCO$^+$ was proposed on the basis of Multi-Reference Configuration Interaction (MRCI) calculations with localized

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orbits. Using a diabatization 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 diabatization procedure, calling the DR of HCO + an “enigma” and proposing instead a “multi-step mechanism” for DR of HCO +, where the electron capture and dissociation proceed through a series of $\Delta \mu = 1$ 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 ($X^2A') and first excited (A^2A'\prime$) 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 H$_2^+$ [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 $1.0 a_0 \leq r_{CH} \leq 4.0 a_0$, $1.78 a_0 \leq r_{CO} \leq 2.55 a_0$ 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 reference configurations and 1.2 million single and double excitations. The calculated MRCI potentials

The adiabatic quantum defect $\mu_{l\lambda}$ is related to the energy difference between the potential of the ion ($V_{i\alpha}$) and neutral Rydberg state ($V_{nl\alpha}$) according to Mulliken’s equation $V_{nl\alpha} = V_{i\alpha} - 1/(2(n - \mu_{l\lambda})^2)$, where $V_{nl\alpha} = n - \mu_{l\lambda}$ is the effective quantum number. In the MQDT formalism the quantum defects
Figure 1. Potential energy of the ground state of the HCO$^+$ ion and energies of several excited states of the neutral HCO molecule calculated (a) at linear geometry ($\theta = 180^\circ$) and $r_{CO} = 2.0877 \text{ a}_0$ and (b) as functions of the bending angle, where $r_{CH} = 2.0 \text{ a}_0$ and $r_{CO} = 2.0877 \text{ a}_0$ are fixed. Black squares show the potential of the ion, calculated using MRCI. The filled symbols indicate 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 $r_{CH}$ 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 $r_{CH}$ dependence. The fitted parameters are then splined over $r_{CO}$ 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 $R = r_{CH}$ 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 $\theta$ is the angle between $R$ and $r$. In the adiabatic approximation, the ionic vibrational wave functions are calculated by first solving the Schrödinger
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 cm$^{-1}$ for the lower (020, 001) vibrational modes, but for higher energies the difference increases to a few hundreds of 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

$$S_{\Lambda \Lambda', \nu \nu'}(R) = \left\langle \phi_{\nu \nu'} | S_{\Lambda \Lambda'} | \phi_{\nu' \nu} \right\rangle,$$

where $\phi_{\nu \nu'}$ is the vibrational wave function of the 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 $(\nu, \nu')$ vibrational levels. All resonances are relatively narrow with autoionization widths $\Gamma_i(R) < 1$ 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 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

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

(2)

where $X_k^R(R)$ 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 ($\phi_{v_k}$) to calculate the full S-matrix

$$S_{A_{v_k}v_R, A'_{v_k'}v_R'} = \langle \phi_{v_k} | S_{A_{v_k}v_R, A'_{v_k'}v_R'} | \phi_{v_k'} \rangle.$$

(3)

Then the channel elimination is applied to obtain the physical S-matrix ($S^{\text{phys}}_{f,i}$) 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

$$\sigma(E_{\text{el}}) = \frac{\pi}{2E} \left( 1 - \sum_{f,i} S^{\text{phys}}_{f,i}(E) S^{\text{phys}}_{f,i}(E) \right), \quad E_{\text{el}} = E - E_i,$$

(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 \((\nu_{\text{CH}}, \nu_\theta, \nu_{\text{CO}})\) is the ionic vibrational mode of the resonance. \( \Gamma_{\text{box}} \) is the width calculated using box-states, while \( \Gamma_{\text{Siegert}} \) is calculated using Siegert states. The widths measured by Grant et al [8] are displayed as \( \Gamma_{\text{exp}} \).

| Energy (H) | \( n \) | \((\nu_{\text{CH}}, \nu_\theta, \nu_{\text{CO}})\) | \( \Gamma_{\text{box}} \) (cm\(^{-1}\)) | \( \Gamma_{\text{Siegert}} \) (cm\(^{-1}\)) | \( \Gamma_{\text{exp}} \) (cm\(^{-1}\)) |
|-----------|-------|---------------------------------|-----------------|-----------------|-----------------|
| 8.65 \times 10^{-5} | 6 | (1,0,0) | 1 | 3 | - |
| 3.13 \times 10^{-3} | 7 | (1,0,0) | 3 | 6 | - |
| 2.12 \times 10^{-4} | 7 | (0,0,1) | 0.08 | 2 | 10 |
| 2.30 \times 10^{-3} | 8 | (0,0,1) | 0.026 | 1 | 8 |
| 6.50 \times 10^{-3} | 12 | (1,0,0) | 0.018 | 0.7 | 2.5 |
| 2.30 \times 10^{-4} | 12 | (0,1,0) | 0.013 | 0.6 | 1.5 |
| 7.53 \times 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 Siegert 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 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 Siegert 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 HCO\(^+\).

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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] Lauhé S, Le Padellec A, Sídko 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 J-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, Ostroovsky V N and Nakamura H 1997 Phys. Rev. Lett. 79 2026
   Tolstikhin O I, Ostroovsky V N and Nakamura H 1998 Phys. Rev. A 58 2077