Towards a model for the dissociative recombination of the CO$^{2+}$ dication: states and couplings


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Abstract.

Preliminary results which will be used for calculations of dissociative recombination (DR) of electrons with the CO$^{2+}$ dication are presented. The measurements of CO$^{2+}$ dissociative recombination rates, the first for any multiply charged target, were obtained at the ASTRID heavy ion storage ring. The present study starts from the potential energy curves for the first 7 electronic states of CO$^{2+}$ and results for low-energy e$^-$ – CO$^{2+}$ scattering that were obtained in recent R-matrix calculations (Vinci and Tennyson, J Phys. B, 37 (2004) 2011). Meanwhile, in order to apply an MQDT-type approach that has been previously used for NO$^+$, we concentrate on partial the resonance series converging to the $^1\Delta$ target state in the CO$^+$ $^2\Sigma^+$ symmetry. The quasi-discrete vibrational spectrum of the CO$^{2+}$ ground electronic state is explored.
1. Introduction

Small molecules with more than a single charge are inherently unstable due to Coulomb forces. However it is well established that some dications can live for significant length of time. CO$_2^+$ is a prime example of such a dication and one may well be of astrophysical importance.

Dissociative recombination (DR) provides a possible destruction route for the long-lived metastable states of dications. CO$_2^+$ was the first multiply charged target to have its DR rate measured. These measurements were performed at the ASTRID storage ring [1] and were subsequently repeated using a corrected calibration formula for the absolute scale of rate coefficients [2]. Recently the DR rate has been re-measured using the TSR storage ring [3], confirming the re-calibrated dissociative recombination rate measured previously [2].

Our aim is to study the DR of CO$_2^+$ by combining resonance curves and widths computed with the R-matrix method [5,6] with a Multichannel Quantum Defect Theory (MQDT) approach [7] to the treatment of the nuclear dynamics. Such an approach was used successfully by two of us to study the DR of NO$^+$ [4]. Here we present our progress on this project.

The present work follows a detailed theoretical analysis devoted mainly to the resonant CO$^+$ states and their autoionization widths [6]. This analysis, based on R-matrix calculations, showed that seven CO$_2^+$ states provide the cores of these resonances, and contribute in a coherent way to the autoionization. However, binary interactions between a Rydberg state pertaining to one CO$_2^+$ core (e.g. X $^3\Pi$) and a Rydberg state pertaining to another CO$_2^+$ core (e.g. $^1\Delta$) cannot be evaluated from the resonance width computed in Ref. [6] by a deconvolution procedure.

Therefore, in order to investigate the dissociative recombination dynamics, the R-matrix calculations had to be partly re-launched in order to provide to the MQDT computational procedure [4, 7] with these "channel to channel", or “2-channel” interactions. More specifically, for every pair of ionic cores, we have to perform separate “2-channel”, rather than “7-channel” calculations. Preliminary data, relevant to the DR rates, are presented here. These data arise from the CO$^+$ $^2\Sigma^+$ resonance series converging to the $^1\Delta$ target state only. The choice of these states is based on their favorable crossings with the CO$_2^+$ ground state curve. Low-lying mono-excited $^2\Sigma^+$ CO$^+$ Rydberg states (‘bound states’), relevant to resonant contributions to DR through the ‘indirect process’, are also considered.

2. Molecular Data

The lowest dissociative limit in figure 1 from Ref. [6], C$^+$ ($^2P_u$) + O$^+$ ($^4S_u$), is 35.986 eV above the X$^1\Sigma^+$ state of CO [8,9]. Our energy of the X $^3\Pi$ state of CO$_2^+$ at equilibrium bondlength is $-111.4871$ E$_h$ as calculated using Natural Orbitals (NOs) and a complete active space configuration interaction representation; see Table 1 in [5]. In the above
cited figure, this minimum is fixed to the experimental value [10] in eV. Figure 1 details the $^3\Pi$ and $^1\Delta$ target states dissociation limits as well as the DR atomic limits. Inclusion of the scattering electron leads to resonance series such as those displayed in figure 2. These have been calculated using both the 7-channel target close-coupling expansion used previously and a reduced 2-channel model. It should be noted that figure 2 corrects the energy scale of figure 5 in the work of Vinci and Tennyson [6], for which the unit label was not correct.

![CO$^{2+}$ Potential Energy Curves](image)

**Figure 1.** The atomic dissociative limits of the $^3\Pi$ and $^1\Delta$ states of CO$^{2+}$ are compared with the DR atomic limits that are associated to the $n^{th}$ resonances series in the continuum of CO$^+$.  

3. CO$^{2+}$ ground state vibrational dynamics

To accurately model the CO$^{2+}$ DR, one needs electronic energy potential curves for CO$^{2+}$ and CO$^+$ over a broad range of internuclear distances. Therefore, we extended the CO$^{2+}$ data available from Vinci and Tennyson [6] using those obtained recently by Eland *et al* [11]. Figures 1 and 3 show that the $^3\Pi$ CO$^{2+}$ electronic energy curve displays, as do some of those corresponding to excited states, a barrier at intermediate internuclear distance. This barrier allows the potential to support vibrational states with finite lifetimes with respect to the auto-dissociation. Calculations of the vibrational energy
Figure 2. Resonance positions for the $^2\Sigma^+$ total symmetry for the series converging to the CO$^{2+}$ $^1\Delta$ state. Full curves represent 7-channel calculations and dashed curves 2-channel ones.

Figure 3. The vibrational levels of CO$^{2+}$ in its $^3\Pi$ ground electronic state. The vibrational probability density for the highest vibrational level ($v = 11$) is represented, after multiplication by 40 in the classical forbidden region.
levels and of their lifetimes for the \( \text{CO}^{2+} \) ground state have been performed using a method previously elaborated and tested on the \( \text{CO}^+ \) ion [12]. It relies on the accurate detection of the sudden phase-shift variation characterising the wave-functions \( \chi_N \) of the resonant states in the asymptotic region [13-16]. This behaviour is described essentially by the formulae:

\[
\chi_N(R) = \kappa R [j_N(\kappa R) + \tan \phi_N \cdot n_N(\kappa R)] , \quad R > R_a
\]  

(1)

\[
\kappa = \sqrt{2\mu(E - V_a)/\hbar^2}
\]  

(2)

\[
\phi_N(E) = \arctan \left[ \frac{\kappa j'_N(\kappa R_a) - \gamma_N j_N(\kappa R_a)}{\kappa n'_N(\kappa R_a) - \gamma_N n_N(\kappa R_a)} \right]
\]  

(3)

\[
\gamma_N = \frac{\chi'_N(R)}{\chi_N(R)} \biggm|_{R_a}
\]  

(4)

\[
\phi_N^*(E) = \phi_N^{(0)} + \arctan \frac{\Gamma}{2(E_r - E)}
\]  

(5)

\[
\frac{d\phi_N}{dE} = \frac{\Gamma/2}{(E_r - E)^2 + (\Gamma/2)^2}
\]  

(6)
where $R$ is the internuclear distance, $E_r$ is the resonance (quasi-discrete state) energy, 
$\phi_N$ is the phase-shift – given for a certain rotational number $N$ of the molecular system, 
$\mu$ is the reduced mass, $V_\infty$ the asymptotic limit of the potential curve, $R_n$ represents 
the lower limit of the asymptotic region (for which a reasonable value must be chosen), 
and $j_N$ and $n_N$ are spherical Bessel and Neumann functions respectively. The quasi-
discrete vibrational states are characterised by the resonant behaviour of the phaseshift 
$\phi_N^*$ described by formula (5), corresponding to a Lorentzian form of the phaseshift’s 
derivative as given by formula (6). $\phi_N^{(0)}$ represents the non-resonant, or background, 
part of the phaseshift in the region of the resonance, and the prime $'$ in formulae (3) 
and (4) stands for the derivative of the functions. Finally, $\Gamma$ labels the resonance width, 
from which the lifetime 

$$\tau = \frac{\hbar}{\Gamma} \quad (7)$$ 

is evaluated.

We shall restrict ourselves to rotationally cool dications, and consequently the 
rotational number $N$ will be taken as 0.

The first step in detecting the resonant states is to solve the Schrödinger equation 
for an adjusted potential, where the barrier is absent. Once an approximate value for 
an energy level is determined, we can search for the true resonant energy exploring 
a limited range around this value. Figure 4 shows the behaviour of the phase-shift 
and of its derivative in the resonance region. The procedure is used to determine 
accurately quasi-discrete levels, their widths, see eq. (5), and their wave-functions, 
see Figure 3. The quasi-discrete states are characterised by a significant amplitude 
of the wave-function in the classical allowed region, and a very reduced one in the 
classically forbidden region, which is the opposite behaviour to the that found for "free" 
(continuum) vibrational states. As the energy of a quasibound state decreases so does 
its width and the determination of the resonance energy and width becomes numerically 
difficult. This means that the determination of these characteristics for the ground 
and the first excited states has not so far proved possible, red and it will have to wait for 
a calculation performed using quadruple-precision. Meanwhile, the energies and the 
wave-functions of these low-lying states are quite well described by an approximate 
calculation where the barrier is replaced by a flat potential.

The energy levels, widths and the corresponding lifetimes for $v = 7, 8,...,11$ are 
given in table 1. Also given are their approximate values evaluated within the semi-
classical approximation of Gamow and improved by the quantum correction of Connor 
and Smith [14-16], as well as the values calculated in [11]. The differences between our 
data and those of Eland and co-workers come mainly from the different values of the $^3\Pi$ 
potential curve computed in ref. [6], with respect to those computed in ref. [11], at small 
internuclear distances. Another source of differences is the use of different numerical 
methods used in the two studies for solving the Schrödinger equation.

We notice that a complete carcerisation of the vibrational spectrum, including 
the highly excited vibrational states, is quite important for an accurate DR modelling.
### Table 1.

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^{(0)} ) (a.u.)</td>
<td>0.0415733</td>
<td>0.0459022</td>
<td>0.0500139</td>
<td>0.0538235</td>
<td>0.0571639</td>
</tr>
<tr>
<td>( E ) (a.u.)</td>
<td>***</td>
<td>0.0459023</td>
<td>0.0500141</td>
<td>0.0538236</td>
<td>0.0571596</td>
</tr>
<tr>
<td>( \Gamma_{\text{Gamow}} ) (a.u.)</td>
<td>7.146E−19</td>
<td>3.794E−15</td>
<td>1.007E−11</td>
<td>1.088E−08</td>
<td>4.170E−06</td>
</tr>
<tr>
<td>( \Gamma_{\text{Connor}} ) (a.u.)</td>
<td>7.189E−19</td>
<td>4.001E−15</td>
<td>1.050E−11</td>
<td>1.107E−08</td>
<td>4.157E−06</td>
</tr>
<tr>
<td>( \Gamma ) (a.u.)</td>
<td>***</td>
<td>3.777E−15</td>
<td>9.807E−12</td>
<td>1.090E−08</td>
<td>3.680E−06</td>
</tr>
<tr>
<td>( \Gamma_{\text{Eland}} ) (a.u.)</td>
<td>2.892E−19</td>
<td>2.628E−15</td>
<td>9.651E−12</td>
<td>1.401E−08</td>
<td>6.820E−06</td>
</tr>
<tr>
<td>( \tau_{\text{Gamow}} ) (s)</td>
<td>33.848</td>
<td>6.374E−03</td>
<td>2.401E−06</td>
<td>2.222E−09</td>
<td>5.800E−12</td>
</tr>
<tr>
<td>( \tau_{\text{Connor}} ) (s)</td>
<td>33.647</td>
<td>6.044E−03</td>
<td>2.303E−06</td>
<td>2.184E−09</td>
<td>5.812E−12</td>
</tr>
<tr>
<td>( \tau ) (s)</td>
<td>***</td>
<td>6.403E−03</td>
<td>2.466E−06</td>
<td>2.218E−09</td>
<td>6.572E−12</td>
</tr>
<tr>
<td>( \tau_{\text{Eland}} ) (s)</td>
<td>83.647</td>
<td>9.200E−03</td>
<td>2.506E−06</td>
<td>1.726E−09</td>
<td>3.546E−12</td>
</tr>
</tbody>
</table>

Indeed, although these latter states are involved mainly in the closed ionization channels, their contribution may play an important role in the DR cross-section, due to the channel-mixing effects [17].

The characterisation of the resonant ("quasi-discrete") states will serve as starting point for \( \text{CO}^2+ \) dissociative recombination calculations. On the other hand, the lifetime evaluations can be used in applications related to "volcanic states" as support in energy storage, as previously invoked for the case of the \( \text{He}^2+ \) dication [18].

### 4. Preliminaries for dissociative recombination dynamics and conclusions

Detailed calculations studying the DR dynamics are planned to be performed in Le Havre. These calculations are complicated by the sheer number of curves which have to be considered to model the DR in the system, even at very low electron impact energies. Besides the many curves in the \( ^2\Sigma^+ \) series of \( \text{CO}^+ \) dissociative states illustrated in figure 3, converging to the \( ^1\Delta \) \( \text{CO}^{2+} \) potential, 5 further \( \text{CO}^+ \) series, either of different symmetries, or converging to different \( \text{CO}^{2+} \) limits provide numerous effective dissociative channels. On the other hand, as shown in figure 1, the 3 lowest \( \text{CO}^{2+} \) curves are almost degenerate, providing 3 different target states as possible starting points for the DR reaction.

Furthermore, it is not straightforward to predict the form of all the potential curves and widths involved for internuclear distances beyond \( R = 3 \text{ a}_0 \). This means that further electron scattering calculation may well be necessary.

In conclusion, we have characterised the curves involved in the low-energy...
dissociative recombination of \( \text{CO}^{2+} \) and started to study the nuclear dynamics of the problem. However, a complete model of the \( \text{CO}^{2+} \) DR will require a huge computational effort. So far, our studies have been restricted to the DR of the \( \text{CO}^{2+} \) ground state \( ^3\Pi \) into \( \text{CO}^+ \) \( [^1\Delta\text{(nd)}] \) \( ^2\Sigma^+ \) states. The coupling displayed in Figure 5, as well as the quantum defect characterising the Rydberg series of bound states of \( ^3\Pi \) core will be used in a preliminary partial evaluation of the cross section. Further 2- channel calculations are currently being performed in order to provide all the DR-relevant energies and couplings, necessary for a complete quantitative description of the \( \text{CO}^{2+} \) DR process.

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References


