Rotational and vibrational lifetime of isotopically asymmetrized homonuclear diatomic molecular ions

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Radiative relaxation times of rovibrational transitions for the electronic ground state of HD$^+$, $^{16}$O$^+$, and $^{12}$C$^+$ are calculated. These lifetimes are compared with the storage time in a heavy-ion storage ring where molecular ions can be stored, in order to provide vibrationally and rotationally cold ions. The relevance of the results to the measurement of dissociative recombination of cold molecular ions is discussed.

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I. INTRODUCTION

It is well known that the radiative rovibrational lifetime of molecules is important in several areas of physics, such as in plasmas, and in spectroscopic observations of interstellar clouds where a large number of molecules and molecular ions have been observed [1]. In order to obtain quantitative values for the densities of such species, the transition strength between various rotational-rovibrational levels is of great importance. Moreover, measurements of the microwave spectra of certain molecules (e.g., CO, HCN, H$_2$CO, etc.) in certain interstellar clouds have revealed anomalous enrichment of the rare isotopic species with respect to their terrestrial abundance levels (e.g., for $^{13}$C, $^{15}$N, $^{18}$O, etc.) [2].

Another area where the knowledge of the lifetime of rovibrational transition is important is related to the cooling of internal degrees of freedom of molecules. During the past two years, new types of experiments have been performed in a heavy-ion storage ring [3–7]. In these experiments, molecular ions are stored for a relatively long period of time and thus can be cooled to the ground vibrational and—perhaps—rotational state. Since these molecular ions are produced in a regular ion source (such as a duoplasmatron or sputter source), they are generally highly vibrationally excited. In order to completely relax a molecular ion to the ground state, the storage time of the beam in the ring has to be longer than the typical decay time for rovibrational transition. For molecules with an electric dipole moment such as diatomic heteronuclear molecules, these decay times are in the range of milliseconds to a few seconds. Clearly, this technique of radiative relaxation is inapplicable for molecules with no dipole moment. As an example, the estimated lifetime for the quadrupole transition from $v=1$ to $v=0$ in H$_2^+$ is of the order of $10^6$ s [8].

Among the various molecular ion experiments which can be performed using the heavy-ion storage ring technique, the first have focused on the process of dissociative recombination between electrons and molecular ions [3–7]. In this process, a molecular ion $AB^+$ captures an electron in one of the dissociative states and dissociates into two neutral fragments $A+B$. It is well known that the cross section for this process is very sensitive to the initial vibrational (and rotational) state of the molecular ion $AB^+$ [9]. The dissociative recombination cross section has been measured over the past 20 years for a great variety of molecular ions; a review of this field can be found in Ref. [10]. Various methods have been used to measure the cross section, but the most successful one has been the merged beam technique [10]. In these experiments, a beam of molecular ions is produced in an ion source, accelerated to an energy of several hundreds keV, and merged with an electron beam. The relative energy in the frame of reference of the molecular ions can be varied by detuning the electron beam energy and the neutralized fragments can be collected after the interaction region. Various types of ion sources have been used in order to produce internally cold beams of molecular ions [11]; however, it is very difficult to measure the population of the various vibrational states and some uncertainties still remain as to whether the ions are fully relaxed.

Using the heavy-ion storage ring technique, a beam of molecular ions can be stored for a long period of time (beam lifetimes varying from a few seconds up to a minute), after acceleration to an energy of several MeV, thus allowing for the deexcitation of the initial vibrational and rotational excitation. This technique is valid only if all the vibrational modes are infrared active. Since homonuclear diatomic ions do not possess a dipole moment, no vibrational cooling is possible via dipole transitions. However, a homonuclear diatomic ion that has been asymmetrized by isotopic enrichment possesses a dipole moment relative to the center of mass (because the center of mass and center of charge do not coincide [12,13]). Such molecules (such as H$_2^+$, O$_2^+$, and C$_2^+$) are among the most interesting cases for the dissociative recombination process, thus it is interesting to know if it is possible to vibrationally and rotationally relax asym-
metrized homonuclear diatomic ions by storing them in a storage ring. In the following, we present estimates of the lifetimes of rotational and vibrational transitions for the isotopically asymmetric diatomic ions HD+, $^{16}$O$^{18}$O+, and $^{12}$C$^{13}$C+ and a comparison with their measured or estimated storage time at the Test Storage Ring (TSR) located at the Max Planck Institut für Kernphysik, Heidelberg [14].

II. METHOD

The radiative lifetimes of rovibrational states were estimated for the electronic ground state of several isotopically asymmetric diatomic ions within the following approximations: (i) The Born-Oppenheimer approximation is assumed to be valid, (ii) the rotational-vibrational coupling is not included, and (iii) only electric dipole transitions are taken into consideration.

The radiative lifetime $\tau_{\nu',j'}$ of a rovibrational state $\nu'J'$, where $\nu'$ and $J'$ are the vibrational and rotational quantum numbers, is given by

$$\tau_{\nu',j'} = \frac{1}{A_{\nu',j'}} ,$$

where $A_{\nu',j'}$ is the total Einstein coefficient, which in the present case is the sum over all probabilities for spontaneous transitions between any two rovibrational states, in the ground electronic state. The spontaneous radiative transition probability between two specific states $\nu'J'$ and $\nu''J''$, usually expressed as the Einstein coefficient $A_{\nu',j';\nu'',j''}$, is given by

$$A_{\nu',j';\nu'',j''} = 7.2356 \times 10^{-6} \Delta E_{\nu',j';\nu'',j''} |M_{\nu',j';\nu'',j''}|^2,$$

where $\Delta E_{\nu',j';\nu'',j''}$ is the energy difference between the two states. If $\Delta E$ is given in cm$^{-1}$ and $M_{\nu',j';\nu'',j''}$ in $\text{e\,\AA}$, then $A_{\nu',j';\nu'',j''}$ is in units of s$^{-1}$.

The total Einstein coefficient $A_{\nu',j'}$ is given by

$$A_{\nu',j'} = \sum_{\nu'',j''} A_{\nu'',j''} ,$$

where

$$A_{\nu'',j''} = C \frac{(J''+1)^2 - \Lambda^2}{(2J''+1)} \sum_{\nu'\nu''} |\mu_{\nu'\nu''}|^2 \Delta E^3_{\nu',j';\nu'',j''} ,$$

and $C$ is the numerical factor as in Eq. (2). $\Lambda$ is the quantum number of the electronic angular momentum about the internuclear axis and is determined by Hund's coupling rules [17] (see Sec. III).

The dipole matrix element is given by

$$\mu_{\nu',j'} = \int_0^{\infty} \psi_{\nu'}(R) \mu(R) \psi_{\nu'}(R) dR ,$$

where $R$ is the internuclear distance, $\psi_{\nu'}$ and $\psi_{\nu''}$ are the vibrational parts of the wave functions, and $\mu(R)$ is the dipole moment function.

The dipole moment function of a homonuclear diatomic molecular ion of charge $Q = Ze$ containing isotopes of masses $m_1$ and $m_2$ separated by a distance $R$ is given by

$$\mu(R) = Ze \frac{m_1 - m_2}{m_1 + m_2} R .$$

Note that this expression is exact within the Born-Oppenheimer approximation and is valid irrespective of the electronic state of the molecule.

The energy difference $\Delta E_{\nu',j';\nu'',j''}$ is given by

$$\Delta E_{\nu',j';\nu'',j''} = \Delta E^{\text{ vib}}_{\nu',j'} + \Delta E^{\text{ rot}}_{\nu',j'},$$

where $\Delta E^{\text{ vib}}_{\nu',j'}$ and $\Delta E^{\text{ rot}}_{\nu',j'}$ are the vibrational and rotational energy differences, respectively, and $B_e$ is the rotational constant. The vibrational energy levels and the corresponding wave functions were calculated by solving the Schrödinger equation [18] for the potential curve $V(R)$ of the electronic ground state of the molecular ions. Exact values of the potential curve were used if available from previous calculations. In other cases, a Morse-type potential was used according to the known molecular constants $D_e$, $\omega_e$, and $R_e$ [19].

III. RESULTS

The estimated rovibrational radiative lifetimes of HD+, $^{16}$O$^{18}$O+, and $^{12}$C$^{13}$C+ are given in Tables I, II, and III, respectively, for vibrational levels $\nu \leq 10$. Results for higher vibrational states are not presented since it is known that the Morse approximation to the potential curve is not precise enough for these states. Moreover, the simple Born-Oppenheimer approximation used in this calculation breaks down for these levels. For a given electronic ground state, the value of $\Lambda$ and the relevant values of the rotational quantum number $J'$ were determined by the Hund's coupling case [17] of this state. The $X^2\Sigma_g^+$ state of HD+ and the $X^2\Sigma_g^+$ state of $^{12}$C$^{13}$C+ were considered as Hund case (b) and the $X^2\Pi_{1/2,g}$ state of $^{16}$O$^{18}$O+ as Hund case (a). It is important to point out that the different types of Hund's coupling affect mainly the lifetime of pure rotational transitions.

The results for the $X^2\Sigma_g^+$ state of HD+ are shown in Table I. For this case, exact values of the potential curve have been calculated [20] and were used in the present calculation. The Schrödinger equation was solved for the vibrational energies and good agreement was found with the known experimental results [21]. The calculated lifetimes are in good agreement (within 10%) with calculations based on previous accurate theoretical results of Colbourn and Bunker [22]. The longest vibrational life-
TABLE I. Radiative lifetimes $\tau_{\nu J'}$ (in s) calculated for various rovibrational states $\nu J'$ of the $X^2\Sigma^+_g$ state of HD$^+$.  

<table>
<thead>
<tr>
<th>$\nu=0$</th>
<th>$\nu=1$</th>
<th>$\nu=2$</th>
<th>$\nu=3$</th>
<th>$\nu=4$</th>
<th>$\nu=5$</th>
<th>$\nu=6$</th>
<th>$\nu=7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J'=0$</td>
<td>140.24</td>
<td>14.61</td>
<td>4.04</td>
<td>1.64</td>
<td>0.823</td>
<td>0.469</td>
<td>0.292</td>
</tr>
<tr>
<td>$J'=1$</td>
<td>0.059</td>
<td>0.032</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>$J'=2$</td>
<td>0.032</td>
<td>0.023</td>
<td>0.019</td>
<td>0.016</td>
<td>0.015</td>
<td>0.014</td>
<td>0.011</td>
</tr>
<tr>
<td>$J'=3$</td>
<td>0.023</td>
<td>0.023</td>
<td>0.019</td>
<td>0.016</td>
<td>0.015</td>
<td>0.014</td>
<td>0.010</td>
</tr>
<tr>
<td>$J'=4$</td>
<td>0.019</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0.015</td>
<td>0.014</td>
<td>0.010</td>
</tr>
<tr>
<td>$J'=5$</td>
<td>0.016</td>
<td>0.015</td>
<td>0.014</td>
<td>0.014</td>
<td>0.013</td>
<td>0.013</td>
<td>0.010</td>
</tr>
<tr>
<td>$J'=6$</td>
<td>0.015</td>
<td>0.014</td>
<td>0.013</td>
<td>0.013</td>
<td>0.012</td>
<td>0.012</td>
<td>0.009</td>
</tr>
<tr>
<td>$J'=7$</td>
<td>0.014</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.011</td>
<td>0.011</td>
<td>0.009</td>
</tr>
</tbody>
</table>

TABLE II. Radiative lifetimes $\tau_{\nu J'}$ (in s) calculated for various rovibrational states $\nu J'$ of the $X^2\Pi_{1/2,3/2}$ state of $^{16}$O$^{16}$O$^+$. Numbers in square brackets denote multiplication by powers of 10.  

<table>
<thead>
<tr>
<th>$\nu=0$</th>
<th>$\nu=1$</th>
<th>$\nu=2$</th>
<th>$\nu=3$</th>
<th>$\nu=4$</th>
<th>$\nu=5$</th>
<th>$\nu=6$</th>
<th>$\nu=7$</th>
</tr>
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<tbody>
<tr>
<td>$J'=\frac{3}{2}$</td>
<td>25.06</td>
<td>25.06</td>
<td>25.06</td>
<td>25.05</td>
<td>25.04</td>
<td>25.03</td>
<td>25.02</td>
</tr>
<tr>
<td>$J'=\frac{5}{2}$</td>
<td>12.90</td>
<td>12.90</td>
<td>12.90</td>
<td>12.89</td>
<td>12.89</td>
<td>12.89</td>
<td>12.88</td>
</tr>
<tr>
<td>$J'=\frac{7}{2}$</td>
<td>8.85</td>
<td>8.85</td>
<td>8.85</td>
<td>8.85</td>
<td>8.85</td>
<td>8.85</td>
<td>8.84</td>
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<tr>
<td>$J'=\frac{9}{2}$</td>
<td>6.84</td>
<td>6.84</td>
<td>6.84</td>
<td>6.84</td>
<td>6.84</td>
<td>6.84</td>
<td>6.83</td>
</tr>
<tr>
<td>$J'=\frac{11}{2}$</td>
<td>5.64</td>
<td>5.64</td>
<td>5.64</td>
<td>5.64</td>
<td>5.63</td>
<td>5.63</td>
<td>5.63</td>
</tr>
<tr>
<td>$J'=\frac{13}{2}$</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
</tr>
</tbody>
</table>

TABLE III. Radiative lifetimes $\tau_{\nu J'}$ (in s) calculated for various rovibrational states $\nu J'$ of the $X^4\Sigma^-_u$ state of $^{12}$C$^{13}$C$^+$. Numbers in square brackets denote multiplication by powers of 10.  

<table>
<thead>
<tr>
<th>$\nu=0$</th>
<th>$\nu=1$</th>
<th>$\nu=2$</th>
<th>$\nu=3$</th>
<th>$\nu=4$</th>
<th>$\nu=5$</th>
<th>$\nu=6$</th>
<th>$\nu=7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J'=1$</td>
<td>78.12</td>
<td>78.12</td>
<td>78.11</td>
<td>78.10</td>
<td>78.08</td>
<td>78.05</td>
<td>78.01</td>
</tr>
<tr>
<td>$J'=2$</td>
<td>40.09</td>
<td>40.08</td>
<td>40.08</td>
<td>40.08</td>
<td>40.07</td>
<td>40.06</td>
<td>40.04</td>
</tr>
<tr>
<td>$J'=3$</td>
<td>27.43</td>
<td>27.43</td>
<td>27.43</td>
<td>27.42</td>
<td>27.42</td>
<td>27.41</td>
<td>27.41</td>
</tr>
<tr>
<td>$J'=5$</td>
<td>17.35</td>
<td>17.35</td>
<td>17.35</td>
<td>17.35</td>
<td>17.35</td>
<td>17.34</td>
<td>17.34</td>
</tr>
<tr>
<td>$J'=7$</td>
<td>13.08</td>
<td>13.08</td>
<td>13.08</td>
<td>13.08</td>
<td>13.08</td>
<td>13.07</td>
<td>13.07</td>
</tr>
<tr>
<td>$J'=8$</td>
<td>11.76</td>
<td>11.76</td>
<td>11.76</td>
<td>11.76</td>
<td>11.76</td>
<td>11.76</td>
<td>11.75</td>
</tr>
<tr>
<td>$J'=9$</td>
<td>10.75</td>
<td>10.75</td>
<td>10.75</td>
<td>10.75</td>
<td>10.74</td>
<td>10.74</td>
<td>10.74</td>
</tr>
<tr>
<td>$J'=10$</td>
<td>9.95</td>
<td>9.95</td>
<td>9.94</td>
<td>9.94</td>
<td>9.94</td>
<td>9.94</td>
<td>9.93</td>
</tr>
</tbody>
</table>
time is for the lowest transition ($\nu' = 1$ to $\nu'' = 0$), which is of the order of 60 ms. Thus one can assume that HD$^+$ is fully vibrationally relaxed after a time which is shorter than 1 s. This, however, is not true for rotational transitions, which take place in the lowest vibrational level ($\nu'' = 0$), where the time needed for full rotational relaxation is longer than 2 min.

Measurements of dissociative recombination of HD$^+$ with electrons have been performed using the TSR. Beams of HD$^+$ with energies of 2.5 and 8 MeV have been stored in the ring [3,4] (average vacuum of $5 \times 10^{-11}$ mbar), with a beam lifetime of 5 and 23 s, respectively. It is important to point out that due to the very large cross section ($\sigma \approx 10^{-14}$ cm$^2$) for the process of recombination, even very weak beam currents can be used for these measurements. Thus, even if the beam lifetime is of the order of several seconds, the effective time that such a beam can be stored in the ring, before performing the recombination measurement, is close to 1 min. In any case, it is clear that the HD$^+$ molecules are vibrationally relaxed in a time which is shorter than 1 s. However, since the rotational lifetimes are much longer, the molecular ions were not fully rotationally relaxed in these previous experiments. Future measurements of the recombination rate as a function of storage time (for times longer than 1 s) could help to extract the influence of the rotations on the cross sections. Such effects have been predicted [23,24], but no experimental evidence exists. On the other hand, by measuring the recombination rate for very short storage times (< 1 s), the dependence of the cross section on the vibrational excitation can be extracted. Such a dependence has been observed with HD$^+$ [4,25] and is shown in Fig. 1. A very sharp decrease of the recombination rate is observed for a storage time shorter than 0.3 s. This fast decay is due to the sensitivity of the dissociative recombination process to the vibrational excitation.

Hence it is expected that the recombination cross section will decrease with a time constant comparable to that of the vibrational relaxation. From Table I one can see that the calculated full vibrational relaxation time for HD$^+$ is of the same order of magnitude. Assuming that the initial vibrational state distribution can be approximated by a Franck-Condon distribution [26], one can compute the total relaxation time. The result of such a calculation is in good agreement with the measured 300 ms. A comparison with the same measurement made with H$_3^+$ (see Fig. 1) shows clearly the effect of the radiative relaxation. More details concerning these results can be found in Refs. [3,4].

Results for the rovibrational lifetime for the $X^2\Pi_{1/2,3/2}$ state of $^{16}$O$^{18}$O$^+$ and for the $X^2\Sigma_g^+$ state of $^{12}$C$^{13}$C$^+$ are presented in Tables II and III, respectively. In these cases, a Morse-type potential was used according to the known molecular constants [12,27–29]. Good agreement (within 1%) between the vibrational energies calculated here and previous calculations and observations [27,29] was found for both cases. The vibrational transition times in these cases are much longer than for HD$^+$, and the time scale for full vibrational relaxation of these ions is of the order of few minutes.

Measurements made with a C$_2^+$ beam at the TSR [30] have shown that at the highest possible storage energy of 3.9 MeV, the lifetime of the beam is about 5 s (average vacuum pressure $7 \times 10^{-11}$ mbar), although as pointed out in the HD$^+$ case, the cross section for recombination is so large that an effective storage time of 1 min is possible. However, as can be seen from Table III, this is barely enough for partial vibrational relaxation.

For the $^{16}$O$^{18}$O$^+$ case, the situation is slightly better since the vibrational transition times are shorter by a factor of 3 than for $^{12}$C$^{13}$C$^+$. Thus, assuming that the lifetime of an O$_2^+$ beam is of the same order as for C$_2^+$, one can expect to produce beams of fully vibrationally relaxed molecular ions of oxygen at the TSR. Measurements of the recombination rate of $^{16}$O$^{18}$O$^+$ with electrons will be performed at the TSR in the near future. From the results shown in Tables II and III, no rotational relaxation can be expected, since the storage times are many order of magnitude shorter.

The above results are based on pure rovibrational radiative transitions. Although it is expected that this is the main relaxation process, other possibilities exist. For example, low-lying electronic states could play a role in the deexcitation of high vibrational states. In this case, a transition from a high vibrational state of the electronic ground state to a low vibrational state of the low-lying excited electronic state could be followed by an electronic transition to a low vibrational state of the ground electronic state. Such a transition exists for $^{16}$O$^{18}$O$^+$ involving the $a^4\Pi_u$ excited state, which decays to the $X^4\Pi_g^+$ ground state in about 100 ms [31].

**FIG. 1.** Rate of recombination as a function of storage time for HD$^+$ and H$_2^+$. The fast decay of the HD$^+$ rate is due to vibrational relaxation. The slow decay (both for H$_2^+$ and HD$^+$) is due to particle loss by remanent gas collisions.

**IV. CONCLUSIONS**

From the above results, a complete cooling to the vibrational and rotational ground state of HD$^+$ can be achieved by storing the beam in a heavy-ion storage ring.
For $^{16}\text{O}^{18}\text{O}^+$, cooling to the vibrational ground state is possible, while for the $^{13}\text{C}^{13}\text{C}^+$ case, relaxation to low vibrational states ($v' = 0, 1, 2$) can be achieved. No rotational cooling is expected for these heavy molecular ions in the existing storage time range. Although the beam lifetime was measured at the TSR, no significant change in the results is expected for other existing heavy-ion storage rings. Rotational lifetimes of other asymmetricized homonuclear diatomic molecular ions are available from the authors.

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