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METASTABLE IONS IN THE MASS SPECTRA OF N₂, NO, N₂O, AND NO₂

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Except for a report by Kupriyanov on the existence of a metastable dissociation in CO⁺⁺, no metastable ions have been reported in the mass spectra of diatomic molecules. Metastable ions have been studied in the mass spectra of the triatomic species CO₂, N₂O, NO₂, and H₂S. Using a CEC Model 21-103B mass spectrometer which was modified to increase the pumping speed in the analyzer tube, to increase the sensitivity of the D.C. amplifier, and to accurately measure potentials applied to the metastable suppressor, metastable ions have been observed in the mass spectra of N₂ and NO. In N₂O and NO₂, metastable dissociation of N₂⁺ and NO⁺ were also observed.

Metastable peaks which have been observed in these molecules are:
1) N₂⁺ → N⁺ + N (M/q) = 7.00 from N₂ and N₂O
2) NO⁺ → O⁺ + N (M/q) = 8.53 from N₂, N₂O, and NO₂
3) N₂O⁺⁺ → N⁺ + NO⁺ (M/q) = 8.91
4) N₂O⁺ → NO⁺ + N (M/q) = 20.45
5) NO₂⁺ → NO⁺ + O (M/q) = 19.57

Each of these transitions has been shown to proceed by a unimolecular mechanism.

Half lives for the metastable dissociations have been studied by various methods. For reaction (3), studies on an AEI-MS9 high resolution instrument with an ion transit time from source to collector of about 7 μsec, showed that no N₂O⁺⁺ ions exist (<10⁻⁶ of N₂⁺ intensity) at that time after formation. Therefore M/q = 22 in N₂O represents N₂O⁺⁺ plus CO⁺⁺ background and a half life of N₂O⁺⁺ is obtainable from an ion-accelerating voltage discrimination curve of the intensity of M/q = 22. A value of t₁/₂ = 0.46±0.05 μsec was found. For the other transitions, especially those in Eqs. (1) and (2), the method of Hipple could not be applied owing to the low intensity of these peaks even under the best conditions of focus. Therefore accelerating voltage discrimination curves of the intensity of the metastable peak were compared to computer calculated curves in assessing the half lives.

Kinetic energy release in the metastable dissociation was evaluated from the width of the metastable suppressor cutoff curves of the metastable ion peak.

The Tables I, II, and III give data on these transitions as a function of the source of the metastable ion.

Table I. Data for the transition N₂⁺ → N⁺ + N, (M/q) = 7.00, with source of N₂⁺.

<table>
<thead>
<tr>
<th>Source</th>
<th>N₂</th>
<th>N₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂ (μsec)</td>
<td>20.15</td>
<td>20.15</td>
</tr>
<tr>
<td>T (eV)</td>
<td>0.55±0.10</td>
<td>0.20±0.05</td>
</tr>
<tr>
<td>AP (eV, obs.)</td>
<td>24.9±0.3</td>
<td>27.5±0.5</td>
</tr>
<tr>
<td>AP (eV, calc.)</td>
<td>24.85</td>
<td>26.18</td>
</tr>
<tr>
<td>ΔAP (obs. - calc.)</td>
<td>---</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Table II. Data for the transition NO$^+ + O^+ + N$, ($M/q)^* = 8.53$, with source of NO$^+$.

<table>
<thead>
<tr>
<th>Source</th>
<th>NO</th>
<th>N$_2$O</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{1/2}$ (µsec)</td>
<td>20.18</td>
<td>20.18</td>
<td>20.18</td>
</tr>
<tr>
<td>T (eV)</td>
<td>0.04±0.02</td>
<td>0.13±0.03</td>
<td>0.13±0.13</td>
</tr>
<tr>
<td>AP (eV, obs.)</td>
<td>20.2±0.2</td>
<td>27.5±0.5</td>
<td>24.6±0.5</td>
</tr>
<tr>
<td>AP (eV, calc.)</td>
<td>20.14</td>
<td>25.16</td>
<td>23.35</td>
</tr>
<tr>
<td>ΔAP (obs. - calc.)</td>
<td>~2.3</td>
<td>~1.3</td>
<td>~1.3</td>
</tr>
</tbody>
</table>

Table III. Data for miscellaneous transitions in N$_2$O and NO$_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>N$_2$O$^{++} + N +$</th>
<th>N$_2$O$^{++} + NO^+ + N$</th>
<th>NO$_2^+$ + NO$^+ + 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>($M/q)^*$</td>
<td>8.91</td>
<td>20.45</td>
<td>19.57</td>
</tr>
<tr>
<td>$t_{1/2}$ (µsec)</td>
<td>0.46±0.05</td>
<td>0.09±0.01 [0.7]a</td>
<td>[0.7]a</td>
</tr>
<tr>
<td>T (eV)</td>
<td>6.5±0.5</td>
<td>[1.0]*±0.05</td>
<td>[1.1]</td>
</tr>
<tr>
<td>AP (eV, obs.)</td>
<td>36.5±0.5</td>
<td>15.7±0.5</td>
<td>12.6±0.3 (w)</td>
</tr>
<tr>
<td>AP (eV, calc.)</td>
<td>35.2</td>
<td>15.23</td>
<td>12.86 (w) [0.5]</td>
</tr>
<tr>
<td>ΔAP (obs. - calc.)</td>
<td>~1.3</td>
<td>~0.5</td>
<td>~1.3</td>
</tr>
</tbody>
</table>

aBracketed figures are from Ref. 6.

In Table I, for N$_2^+ + N^+ + N$, the half life is seen to be independent of source but the kinetic energy release changes from 0.55 eV from N$_2$ as a source to 0.20 eV from N$_2$O as a source. From N$_2$ the observed AP equals that calculated from the dissociation limits, but from N$_2$O as a source, about 1.3 eV of energy is unaccounted for. It is assumed that this is kinetic energy released in the initial fast fragmentation of N$_2$O$^+ + (N$_2^+)$ + 0. A similar situation exists in the metastable dissociation NO$^+ + O^+ + N$, in the mass spectra of N$_2$O and NO$_2$.

In regard to the mechanism of the metastable dissociation, three mechanisms are considered. 1) A slow radiation from a higher bound state to a dissociative state. The half life is then the radiation lifetime. This is impossible in Eqs. (1) and (2) since with N$_2$ and NO as sources, the calc. and obs. AP's are equal, leaving no energy for radiation. 2) A tunneling mechanism through a low barrier to dissociation. In N$_2^+ + N^+ + N$ from N$_2$ and N$_2$O sources, the difference in T would imply a difference in half life of at least a factor of 100 for tunneling. Since the half lives are essentially equal, this mechanism can be discarded. 3) A predissociation mechanism in which a bound state is crossed by a repulsive state. The crossing must be a forbidden one. In NO$^+ + O^+ + N$, the state in NO$^+$ is probably an unknown higher triplet which is crossed by the $^5L$ state to the dissociation limit at 20.101 eV. In N$_2^+ + N^+ + N$, possible states of N$_2^+$ are the $^2I_u^-$, $^2A_u^-$ and $^2D_u$ states with a forbidden crossing of the $^{11}D_u$ state to the 24.301 eV dissociation limit. All of the bound states radiate to the D $^{11}D_u$ state by allowed transitions but the radiation would be of low energy (<3 eV) hence have a long half life.

The dissociation of N$_2$O$^{++}$ may proceed by mechanism 1), with the half life being determined by the radiation lifetime of ~1.3 eV radiation from a bound state to a repulsive state of N$_2$O$^{++}$.
Footnotes and References

1. This work was performed under the auspices of the U. S. Atomic Energy Commission.
8. The authors thank Dr. R. M. Teeter of Chevron Research Company for this determination.
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