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TRANSLATIONAL SPECTROSCOPY
OF THE UNIMOLECULAR DISSOCIATION

\[ N_2^+ \rightarrow N^+ + N \]

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Résumé. — On observe des structures très prononcées dans le spectre d'impulsion des fragments \( N^+ \) provenant de la dissociation d'ions moléculaires \( N_2^+ \) en l'absence de gaz cible. Ces structures sont attribuées à la dissociation unimoléculaire d'états métastables de \( N_2^+ \) de longue durée de vie (6 \( \times 10^{-8} \) à 3 \( \times 10^{-4} \) s). Les effets isotopiques sont discutés.

Abstract. — An analysis is made of the momentum distribution of forward- and backward scattered \( N^+ \) fragments, produced in the dissociation of \( N_2^+ \) from 5 keV ion beams at residual gas pressure. The pronounced structure observed is ascribed to the unimolecular dissociative decay of metastable states of \( N_2^+ \) having lifetimes between 6 \( \times 10^{-8} \) and 3 \( \times 10^{-4} \) s. Isotope effects are found to be strong. Possible interpretations of the observed (pre)dissociations are discussed.

I. Introduction. — We have recently reported a high-resolution mass spectrometric investigation of the collision-induced dissociation of fast \( N_2^+ \) ions [1]. In this paper we present new results regarding a similar study at a residual pressure \( p \approx 10^{-6} \) torr of the process:

\[ N_2^+ \rightarrow N^+ + N \]  \hspace{1cm} (1)

Some of the data were briefly discussed at the VII ICPEAC [2].

The dissociation of \( N_2^+ \) ions having reached their full acceleration potential gives rise to a diffuse peak in the mass spectrum at an apparent mass [3]:

\[ m_{\text{app}} = \frac{(m_{N^+})^2}{m_{N_2^+}} \]  \hspace{1cm} (2)

Other investigators have attributed at least part of this « dissociation peak » to the predissociation of metastable \( N_2^+ \) ions formed in the ion source [4]-[6], the term « metastable » generally denoting ions having apparent lifetimes of the order of \( 10^{-7} \) to \( 10^{-5} \) s [4]-[7]. These lifetimes, \( \tau \), are apparent ones because of the possibility of cascade processes from higher long-lived states.

II. Experimental. — The apparatus has been described earlier [8]. It comprised a unoplasmatron ion source, an accelerating and focussing system, a 187 cm long drift region and a 180° inhomogeneous analysing magnet. A 3.5 cm long collision chamber was placed 30 cm after the first collimator (\( \varnothing = 0.4 \) mm). The energy spread of the primary ion peaks was about 2 eV; the ion beam was collimated within a solid angle of \( 5.6 \times 10^{-6} \) sr. The spectra were obtained at an accelerating potential \( V_0 \) of 5 kV.

The ions were extracted from the source at about 90 % of the total accelerating potential, and reached their final energy 2.9 \( \times 10^{-7} \) s after extraction, 5 cm upstream of the first collimator. The mean residence time of the metastable particles in the source is difficult to evaluate. If it is neglected, flight-time considerations show that metastable \( N_2^+ \) states whose unimolecular fragmentation could be detected at an apparent mass given by eq. (2) (cf. [7]), were those with lifetimes \( 6 \times 10^{-8} \leq \tau \leq 3 \times 10^{-4} \) s, the optimum value being \( \tau \approx 10^{-6} \) s. If the residence time is estimated to be 5 \( \times 10^{-6} \) s, the optimum is shifted to \( \tau \approx 6 \times 10^{-6} \) s, and the lower limit to about \( 10^{-6} \) s. These numbers are based on the assumption that the observed fragments are formed in the
free-flight region preceding the exit of the collision chamber: fragments formed later on would not give rise to structure in their momentum spectra as sharp as found in the present experiments. The lifetime ranges quoted correspond to the decay of $\gtrsim 1\%$ of the fully accelerated metastables relative to the fraction found for metastables with optimum lifetimes. Provided, of course, that dissociative decay competed effectively with radiative de-excitation, lifetimes between $6 \times 10^{-8}$ s and $3 \times 10^{-4}$ s should be considered « acceptable » in the present context.

The following source gases were used: natural N$_2$ and N$_2$O (« Air Liquide », 99.998 % and 99.99 % purity, respectively); $^{15}$N$^{15}$N (« Azote et Produits Chimiques, 99 % $^{15}$N); $^{14}$N$^{15}$N prepared by pyrolysis and subsequent reduction of $^{15}$NH$_4$$^{14}$NO$_3$ (« Isomel Corporation », 99.2 % $^{15}$N in the NH$_4$ group); and a fifty-fifty mixture of $^{14}$N$^{14}$N and $^{15}$N$^{15}$N.

III. Results. — Figure 1 shows a scan of the mass spectrum between $m_{\text{app}} \approx 6.5$ and $m_{\text{app}} \approx 8$, obtained with the mixture of $^{14}$N$^{14}$N and $^{15}$N$^{15}$N as source gas. N$^+$ fragments produced in (1) and having the same velocity as the parent N$_2$ appear at $m_{\text{app}} = 6.76$, 7, 7.5 and 7.76, depending on the isotope considered. In each case, the charged fragments which acquired a momentum $k$ in the centre of mass (CM) system when formed, appear at slightly higher (forward scattering) or lower (backward scattering) velocity (apparent mass). They give rise to signals nearly symmetrical with respect to the $K = 0$ peak (cf. Fig. 2). For the 14-14 and 15-15 isotopes, the latter is superimposed on the primary N$^+$ peak. The momentum (mass) scale was calibrated by changing $V_0$ e. g. from 5 kV to 5.10 kV and observing the resulting shift of the spectrum. The results of this method were consistent with the internal calibration provided by the relative positions of the apparent masses indicated in figure 1.

The total CM energy of the fragments from (1) is given by:

$$W = \frac{K^2}{2\mu},$$

where $\mu$ is the reduced mass of the fragments. $W$ is also equal to the energy separation between the (pre)dissociated level (energy $E$) of N$_2^+$ and the dissociation limit involved (energy $D$): $W = E - D$. Figure 3 shows examples of the intensity distributions $I(W)$ of forward scattered N$^+$ fragments from the three N$_2^+$ isotopes as a function of $W$. They were obtained by applying to the laboratory distributions an apparatus function which accounts for the trans-
formation Jacobian and for the $W$-dependence of the detection efficiency of the apparatus [8]-[10]. For clarity, the smooth contribution which underlies the structure in the spectra, and which is possibly due to collisions on the background gas, has been subtracted out (cf. Fig. 2).

The $W_{\text{peak}}$ values corresponding to the various (sub)maxima in the $I(W)$ distributions are listed in table 1. For each isotope, we first determined the absolute value of $W_{\text{peak}}$ for the most pronounced peak, labeled $h$. The three experimental averages, together with the standard deviation of the measurements, are indicated at the bottom of the table. The difference between the value found for $^{14}\text{N}^{15}\text{N}^+$ and those found for $^{14}\text{N}^{14}\text{N}^+$ and $^{15}\text{N}^{15}\text{N}^+$ are significant at a 80 % and a 95 % confidence level respectively. The $W_{\text{peak}}$ values for the remaining (sub)maxima were obtained by comparing their positions in each $I(W)$ spectrum to that of peak $h$, using the absolute $W_{\text{peak}}(h)$ values just mentioned for normalization. The standard deviations resulting from this procedure are also listed in table I.

By comparing the halfwidths of the $\text{N}^+$ peak and those of the distinct (sub)maxima in the $K$ distributions (cf. Fig. 2), we were able to estimate the true halfwidths, $\Delta K$, of these well-resolved peaks. This estimate is an upper limit because the angular resolution for detection of $\text{N}^+$ fragments is not as good as for detection of primary $\text{N}^+$. For the peak labeled $h$ in figure 2, e.g., we found $\Delta K \approx 1$ a. u. and $\Delta W = K \Delta K/\mu \approx 5 \times 10^{-2} \text{ eV}$. It is probable that a number of close-lying (e. g. rotational) energy levels of $\text{N}_2^+$ contribute to each of the $\text{N}^+$ peaks found in our dissociation spectra; the $W_{\text{peak}}$ values listed in table I should then be interpreted as locating the optimum for fragment detection within each of the corresponding energy ranges.

The information contained in figures 1-3 and in table I, may be complemented by the following observations (henceforth they will be quoted by their respective indices):

a) For the 14-14 isotope, the spectra obtained using natural $\text{N}_2$ and $\text{N}_2\text{O}$ as source gas were essentially identical, although in the latter case the structure was somewhat better resolved (Fig. 2). The $\text{N}^+$ fragments from the three $\text{N}_2^+$ isotopes gave rise to quite different distributions but there was no significant difference between the overall spectra (cf. Fig. 1) obtained using $^{14}\text{N}^{15}\text{N}$ or the $^{14}\text{N}^{14}\text{N}/^{15}\text{N}^{15}\text{N}$ mixture as a source gas;

b) the best resolved spectra were obtained at low source pressures ($\approx 10^{-3}$ torr) and high arc tensions ($\approx 100 \text{ V}$);

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### TABLE I

<table>
<thead>
<tr>
<th>Peak Label</th>
<th>$W_{\text{peak}}$ (eV)</th>
<th>Spectroscopy $W(C^2 \Sigma_g^+)$</th>
<th>$W_{\text{peak}}$ (eV)</th>
<th>Spectroscopy $W(C^2 \Sigma_g^+)$</th>
<th>$W_{\text{peak}}$ (eV)</th>
<th>Spectroscopy $W(C^2 \Sigma_g^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.048 (8) ***</td>
<td>3</td>
<td>0.044 (5)</td>
<td>***</td>
<td>3</td>
<td>0.029 (5)</td>
</tr>
<tr>
<td>$b$</td>
<td>0.110 (11) *</td>
<td>0.116 (39)</td>
<td>**</td>
<td>0.096 (6)</td>
<td>*</td>
<td>3.014 (5)</td>
</tr>
<tr>
<td>$c$</td>
<td>0.235 (5) **</td>
<td>4</td>
<td>0.289 (5)</td>
<td>**</td>
<td>4</td>
<td>0.271 (5)</td>
</tr>
<tr>
<td>$d$</td>
<td>0.334 (4) *</td>
<td>0.303 (8)</td>
<td>**</td>
<td>0.256 (12)</td>
<td>*</td>
<td>4.252 (5)</td>
</tr>
<tr>
<td>$e$</td>
<td>0.428 (3) ***</td>
<td>0.405 (14)</td>
<td>**</td>
<td>0.382 (10)</td>
<td>*</td>
<td>0.449 (4)</td>
</tr>
<tr>
<td>$f$</td>
<td>0.530 (5)</td>
<td>0.508 (5)</td>
<td>0.630 ***</td>
<td>5.486 (5)</td>
<td>5</td>
<td>0.630 ***</td>
</tr>
<tr>
<td>$h$</td>
<td>0.636 ***</td>
<td>0.649 ***</td>
<td>6.742 (5)</td>
<td>0.716 (5)</td>
<td>6</td>
<td>0.630 ***</td>
</tr>
<tr>
<td>$j$</td>
<td>0.898 (7) ***</td>
<td>0.832 (32)</td>
<td>**</td>
<td>0.870 (3)</td>
<td>**</td>
<td>7.094 (5)</td>
</tr>
<tr>
<td>$k$</td>
<td>0.999 (25) *</td>
<td>1.000 (5)</td>
<td>7.971 (5)</td>
<td>7.094 (5)</td>
<td>7</td>
<td>1.164 (5)</td>
</tr>
<tr>
<td>$l$</td>
<td>1.298 (24) **</td>
<td>1.228 (32)</td>
<td>**</td>
<td>1.220 (10)</td>
<td>**</td>
<td>8.122 (5)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1.452 (5)</td>
<td>9</td>
<td>1.417 (5)</td>
<td>9</td>
<td>1.381 (5)</td>
</tr>
<tr>
<td>$m$</td>
<td>1.500 (25) *</td>
<td>1.670 (5)</td>
<td>1.631 (5)</td>
<td>1.593 (5)</td>
<td>10</td>
<td>1.800 (5)</td>
</tr>
<tr>
<td>$n$</td>
<td>1.830 (20) *</td>
<td>1.883 (5)</td>
<td>1.841 (5)</td>
<td>1.800 (5)</td>
<td>11</td>
<td>1.800 (5)</td>
</tr>
<tr>
<td>$h$</td>
<td>Norm. 0.636 (10)</td>
<td>Norm. 0.649 (22)</td>
<td>Norm. 0.630 (17)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
c) raising the background pressure in the apparatus to $10^{-3}$ or $10^{-4}$ torr by throttling the main diffusion pump or by introducing He, Xe or air in the collision chamber resulted mainly in a smoothing of the spectral structure and an increase of the underlying continuous contribution; at rather high pressures in the collision chamber, e. g. $10^{-3}$ torr, quite different spectra were found — those obtained with He as a target are discussed in reference [1];

$d)$ in the 14-14 spectra the resolved contribution due to the «spontaneous» dissociation of N$_2^+$ inside the collision chamber amounted to about 1 % for the peaks labeled $a$, $b$, $d$, $f$ and $h$; no further structure could be resolved in this region which was singled out by applying a potential to the collision chamber (cf. [1]);

$e)$ from the observed shifts of the N$^+$ spectra for the 14-14 and 15-15 isotopes with respect to the N$^{++}$ marker we concluded that the energy loss related to the observed spectra was smaller than 2 eV and probably zero.

IV. Discussion. — It is clear from the above observations that the main part of the structure observed in the present dissociation spectra cannot be attributed to the collisional excitation and subsequent dissociation of low-lying levels of N$_2^+$ (see $c$, $e$). Excited states formed in the ion source or at the very beginning of the extraction region and having lifetimes between $6 \times 10^{-8}$ s and $3 \times 10^{-4}$ s must be involved. For the $^{14}$N$^{14}$N$^+$ isotope, flighttime considerations based on observation $d)$ allow us to specify that the peaks labeled $a$, $b$, $d$, $f$ and $h$ contain significant contributions of metastables with lifetimes $\tau \geq 5 \times 10^{-7}$ s. The fact that the strong peak $j$ is not observed in the collision chamber indicates that it results mainly from the dissociation of N$_2^+$ ions with lifetimes $6 \times 10^{-8} \leq \tau < 5 \times 10^{-7}$ s.

From $b)$ and $c)$ it also appears that the unimolecular dissociation of the above metastables is the most probable explanation of our results. This interpretation has been adopted by several investigators [4]-[6], and the possible mechanisms involved have been discussed by numerous authors (cf. [3]-[7], [11]). One of these mechanisms, radiation from a metastable state to a lower repulsive state, can give rise to sharp structure in the fragment distribution only in rather special cases. Tunneling and, even more so, predissociation can quite readily result in the type of structure reported here. In either case, the probability of production of fragments with a given $W$, will depend on the value of this excess energy. In experiments such as the present ones, charged fragments will be observable within one or more «$W$-windows», determined by the value of the corresponding lifetimes, $\tau(W)$, relative to the range of «accepted» values, viz. $6 \times 10^{-8}$ to $3 \times 10^{-4}$ s. If, for instance, the predissociation of a metastable state occurs with fairly uniform probability over a number of vibrational levels [12], the window may be wide, in which case we can expect to find (sub)maxima in the $I(W)$ distribution of the resulting fragments locating the various vibrational levels involved. The observation of such a vibrational sequences is possible if the rotational population of the parent ion is narrow enough and the vibrational spacing wide enough to prevent a smearing-out of the structure.

Hardly any data are available with which the $W_{\text{peak}}$ values of table I can be compared. Those found for $^{14}$N$^{14}$N$^+$ are compatible with the results of Fournier et al. [6], considering that the resolution achieved in their investigation was not as good, and the range of «accepted» lifetimes somewhat different ($2 \times 10^{-7} - 2 \times 10^{-6}$ s). In addition, the population of metastable states in the present experiments proceeds mainly via ion-molecule reactions (cf. $a)$ above), rather than by direct electron impact as in references [4]-[6]. The similarity between the spectra found with $^{14}$N$^{15}$N and the $^{14}$N$^{14}$N/$^{15}$N mixture as source gas may e. g. be explained by Maier and Murad's recent finding [13] that the production of N$_2^+$ in low-energy reactions between N$^+$ and N$_2$ involves nearly equal contributions of atom transfer and electron transfer collisions. Ion-molecule reactions may also account for the fact that Newton and Sciamanna [4] found different kinetic energy releases, $T$, when using N$_2$ ($T \approx 0.55$ eV) and N$_2$O ($T \approx 0.20$ eV) as source gas, whereas we found very similar spectra in both cases.

Quantitative spectroscopic information on N$_2^+$ states having energy levels above the first N$^+ +$ N limit is available only for the C$^2\Sigma_u^+$ state [14], and this state has been proposed as a possible «metastable» by earlier investigators. It is apparent from table I that most peaks in our spectra do not consistently match the spectroscopic $W$ values for the C state [15], [16], even if a rotational population over an energy range of, say, 50 meV is taken into account. As the lifetimes of the vibrational levels $v \geq 4$ of the C state fall outside the acceptable range [1], [4], the fit which does occur with some of these levels is either fortuitous or must be attributed to a metastable state populating the C state by cascade. Considering the lower limit of $5 \times 10^{-7}$ s mentioned at the beginning of this discussion, even the $v = 3$ level is probably too short-lived to be assigned to the peaks labeled $a$ in $^{14}$N$^{14}$N$^+$ and $^{14}$N$^{15}$N$^+$.

We have attempted to assign our $W_{\text{peak}}$ values to one or more vibrational sequences on the basis of regularities in their spacings and a systematic isotopic displacement. Only part of them could be tentatively rationalized in this manner; they are labeled $a$, $c$, $d$, $f$ and $g$ in table I, and grouped in this fashion they constitute an — incomplete — sequence with spacings of the order of 0.1 eV for each isotope. The
isotopic displacement implied by this assignment can be reasonably well accounted for by assuming that these peaks result from the predissociation of high-lying vibrational levels \((v \approx 14-19)\) of an electronic state whose potential minimum lies about 2.0 eV below the predissociation limit. The isotope effect on the predissociation probability [17] should be fairly important to account for the fact that three of the levels give rise to resolved peaks for only one or two of the \(N_2^+\) isotopes \((a, c, g\) in table I).

We were not able to make a reasonable assignment of the remaining \(W_{\text{peak}}\) values to (an)other vibrational sequence(s). It is quite possible that they essentially localize a set of rather narrow \(W\)-windows. In this case, the seemingly unsystematic behaviour of these peaks may be due to the combined effects of isotopic displacement on the position of the molecular energy levels and on that of the \(W\)-windows (because of changes in \(\tau(W)\), cf. [17]).

V. Conclusion. — We have observed well-resolved structure in the momentum distribution of \(N^+\) fragments resulting from the dissociation of 5 keV \(N_2^+\) ions at residual gas pressure. The corresponding kinetic energy excesses, \(W_{\text{peak}}\), have been determined with a relative accuracy which, for \(W_{\text{peak}} \geq 0.15\) eV, amounts to \(\leq 4\%\). The structure is ascribed to the unimolecular dissociative decay of metastable states of \(N_2^+\) having lifetimes between \(6 \times 10^{-8}\) and \(3 \times 10^{-4}\) s. Further experiments aimed at clarifying the nature of the \(N_2^+\) states involved, viz. measurements of lifetimes and appearance potentials as a function of \(W\), are in progress.

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