JILA REPORT #42

I.
THE DETECTION OF LONG-LIVED EXCITED STATES OF MOLECULES
BY PENNING IONIZATION

II.
ON THE EVIDENCE OF THE $N_2NO^+$ ION

by

V. Carmák

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University of Colorado
Boulder, Colorado
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PART I
THE DETECTION OF LONG-LIVED EXCITED STATES OF MOLECULES
BY PENNING IONIZATION*

by

V. ČERMÁK**

INTRODUCTION

The development of energy-loss measurements of slow electrons in inelastic collisions with molecules has elicited new data on the energies of electronically excited states\(^1^\)-\(^5\). Due to electron exchange, besides optically allowed states, optically forbidden, long-lived states are also excited. It is therefore of interest to have a method for distinguishing between long-lived and short-lived states, especially in cases of diatomic or polyatomic molecules of astrophysical interest.

A method frequently used has been that of spatial separation of the excitation and detection regions\(^6^\)-\(^8\). Only long-lived states (\(\tau \geq 10^{-5}\) sec) could reach the detector because the short-lived states decayed by radiative transitions. The emission of secondary electrons after the arrival of excited particles on the metallic surface was used for the

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detection. If the energy of exciting electrons was varied, a total excitation efficiency curve was obtained corresponding to the sum of the efficiency curves for all long-lived states present. It was not possible to separate the efficiency curves of individual states (or groups of them). The energy of excited states was determined from the onset of secondary electrons current and from breaks on the curves.

The use of Penning ionization of polyatomic molecules\textsuperscript{9,10} for detecting excited neutral particles seems to offer many new possibilities. The reaction is of the type:

\[ X^* + YZ \rightarrow X + YZ^+ + e^- \]  \hspace{1cm} (1)

In general, ionization occurs when the energy of excited particle $X^*$ is greater than or equals the I.P. of molecule YZ. If the molecule YZ is chosen with increasing ionization potential, YZ then serves as a "detector". The energy of an excited state is then given by $\text{I.P.}(M_1) \leq E < \text{I.P.}(M_2)$, where $M_2$ is the un-ionized "detector" molecule and $M_1$ is the ionized molecule with the lower I.P.

The above condition is necessary but not sufficient. In addition, according to the Wigner rule\textsuperscript{11}, total spin should be conserved in reaction (1) and the ionization cross section must be comparable to the cross section for the decomposition of the superexcited neutral molecule YZ** into neutral fragments \textsuperscript{12} by the reaction

\[ X^* + YZ \rightarrow YZ^{**} + X \] \hspace{1cm} (2)

\[ YZ^{**} = Y^* + Z \] \hspace{1cm} (3)
Energetic data obtained using this method differ, however, from those gained in optical or electron spectroscopy where energy absorbed in the Franck-Condon region is always determined. In the present method the energy available is that in the downward transition in a collision which might have an adiabatic character. This energy can be different from the energy absorbed, and the difference accounts for the change in equilibrium separation of the nuclei in the ground and excited states and for the vibrational excitation of the ground state.

Recently, an apparatus was constructed and used for the investigation of Penning ionization of polyatomic molecules in impact with metastable excited noble gas atoms\(^\text{10}\). In this apparatus a beam of atoms excited by electron impact collides with a beam of selected polyatomic molecules, the ions formed are mass analyzed, and the current of parent and fragment ions is measured.

If diatomic or polyatomic molecules are excited rather than noble gases, it is possible to detect their long-lived states, provided that the ionization reaction satisfies the above-mentioned conditions. The method has the following advantages over those previously used:

1) The proper selection of the detector molecules with different I.P. makes the detection energy-sensitive, as only states with sufficient energy are capable of ionizing the detector molecules. A complication arises when associative ionization intervenes, i.e., if the reaction (4) takes place:\(^\text{13}\)

\[
X^* + YZ \rightarrow XYZ^+ + e .
\]  
(4)
Nevertheless, this presents a problem only when a mass analysis of products is not applied.

2) If the detector molecules with successively decreasing I.P. are used, it is possible, in favorable cases, to separate the efficiency curves of individual states (or groups of them), beginning from the highest state.

3) Data on the energy absorbed in the upward vertical transition (Franck-Condon transition) and the downward, probably adiabatic, transition may be obtained simultaneously. The first case applies when the appearance potential of the ions is determined, the second when molecules with different I.P. are used. This last value is, of course, more precise the more molecules with slightly differing I.P. are used.

Experiments along these lines were started in the Mass Spectrometry Department of the Institute of Physical Chemistry of the Czechoslovak Academy of Science in Prague; N₂, H₂, CO, and O₂ molecules were studied and the ions of detector molecules mass analyzed*. No special effort was made to investigate the excitation functions.

It therefore seemed useful to build an apparatus for making a thorough study of the excitation functions. The molecules investigated were again H₂, N₂, CO, and O₂. New long-lived excited states of N₂ and CO were found and the efficiency curves determined. The type of curve in N₂ reveals that one of the ways of producing the high-lying new long-lived state is via the formation of an unstable excited negative

* These results were presented at a JILA colloquium October 6, 1964.
molecular ion, $N_2^-$, by a resonance process.

EXPERIMENTAL

The schema of the apparatus is presented in Fig. 1. Molecules enter the excitation region through a multichannel tube $T_1$ and are excited by electron beam $E$. The electrons are collimated by a magnetic field of the intensity of 1100 Gauss. An electron current of 10–20 μA is used. Charged particles are removed from the molecular beam by the combined effects of the potential on the grid $G_8$ and the electric field between plates $P_1$ and $P_2$. Electrons are prevented from entering the collision region $B$ by keeping the source at a potential of about 45V positive with respect to the collision region. Excited particles enter the collision region through a 2-mm. hole. Positive ions are collected on the very transparent grid $G_c$ which is held at a potential 20 V negative with respect to the collision chamber. Detector molecules enter it through a multichannel tube $T_2$. The suppressor grid $S$ prevents secondary electrons formed by the impact of excited particles on the open cylinder $C$ from entering the collision region. The potential of the cylinder is 10 V positive with respect to the grid.

The pressure in both the excitation and the collision regions is $10^{-3}$ to $10^{-6}$ mm Hg. The number density of molecules in the excitation region was determined through ionizing the gas by 50 eV electrons and collecting the ions formed on the negative-bias plate, attached to the multiple channel tube $T_A$. The number density is:
\[ \eta_\text{M} = \frac{i^+}{i^- l_i \sigma_i} \]

where \( i^+ \) is the total ion current, \( i^- \) is the electron current, \( l_i \) is the ionization path and \( \sigma_i \) is the ionization cross section for 50 eV electrons.

The maximum background pressure measured by the ionization gauge outside these regions is about \( 5.10^{-5} \) mm Hg and corresponds to the introduction of gases at a total flow rate of about 5μl/sec. The apparatus is pumped by a mercury diffusion pump (Edwards 6M3). No bake-out is used.

The ion current to the collector is measured by means of the Cary vibrating reed electrometer. The zero current fluctuations under experimental conditions are \( 5.10^{-15} \) A. The efficiency curves are obtained with a 2D-2 Moseley X-Y recorder.

The apparatus was checked by ionization of detector molecules with noble gas metastables, whose excitation functions were determined in reaction with NO (I.P. 9.2 V) (Fig. 2). The current could easily be raised up to the order of \( 10^{-12} \) A, preferably by increasing the concentration of noble gas atoms in the excitation region. The breaks on the efficiency curve, marked by arrows, are poorly resolved peaks corresponding to resonance-type excitations at the particular energy. For comparison, curves presented by Olmsted, et al.,\textsuperscript{15} and Dorrestein\textsuperscript{6} are presented in Fig. 3.

When molecules rather than noble gas atoms were excited, the ionic currents were smaller, especially with CO, H\(_2\), and O\(_2\). A complication then arises due to elastic scattering of long-lived states on detector
molecules which were introduced into the collision region. Secondary electrons are emitted from the collector grid as the excited particles strike it, and a positive current is measured. Under the poorest conditions this current was as high as 1/4 of the current of positive ions. The efficiency curve had, under such conditions, an onset at the energy belonging to the lowest excitation energy absorbed, even if detector molecules with rather high ionization potential were used (e.g., N₂). For this reason no systematic effort was made to measure the appearance potentials (A.P.) of the ion current, partly also because the electrons had a big energy spread. Corrections were applied when necessary by subtracting the current measured when N₂ was used as a detector molecule.

It was verified that the current of positive ions does not exhibit a second-order dependence on the exciting electron current and on the pressure of molecules in the regions A and B (Figs. 4, 5). Thus only single collisions took place. The deviation from linearity was caused either by the inactivation and scattering of excited molecules by the parent gas (Fig. 5a) or by the detector molecules (Fig. 5b). It was shown previously that the extent of ionization of detector molecules by photons is insignificant¹⁰. The ionization by secondary electrons in the collision region is also negligible, as otherwise the dependence of the ion current on the pressure of the gases excited in the source region would be quadratic.
RESULTS

Hydrogen

According to Table I there exists a long-lived state which is capable of releasing an energy $11.4 \leq E < 11.6$ eV upon collision. The onset of the ion efficiency curve in the reaction with $\text{C}_2\text{H}_2$ and NO (Fig. 6) implies that the long-lived state should be a molecular state*. Moreover, as the curves are practically similar, only one excited state is involved. The excited state is the $C_3^\Pi_u$ state formed after absorption of the energy 11.87 eV\(^{16}\). The difference in energy can plausibly be explained by the position of the $\text{H}_2$ potential curves for the $C_3^\Pi_u$ state and $X_1^\Sigma_g^+$ state. The equilibrium nuclear separation of the $C_3^\Pi_u$ state (1.037 Å) is greater than that of the ground state (0.741 Å). The molecules in the $C_3^\Pi_u$ should therefore be obtained in a vibrationally excited state. When downward transition occurs, the ground state molecules are formed in the vibrationally excited states, too.

The shape of the excitation function is rather uncommon. Its main features are more marked on the curves presented here than on those reported previously\(^{15,16}\).

* If ionization by excited $\text{H}$ atoms formed in dissociation of $\text{H}_2$ molecules were involved the minimal threshold electron energy should be $D(\text{H}_2) + \text{I.P.}(\text{C}_2\text{H}_2) = 4.55 + 11.4 = 15.96$ eV. Moreover, the excited atoms $\text{H}^+$ should have sufficiently long lifetime. The only known metastable $\text{H}$ atoms have the energy of 10.2 eV which is not high enough for the ionization of $\text{C}_2\text{H}_2$ molecules.
The excitation is probably not a single process. The steep rise at the beginning might correspond to a direct transition and the broad peak might be an excitation of higher lying states which can radiate to the $^3\Pi_u$ state.

Nitrogen

The long-lived species in the beam of $N_2$ yielded after de-excitation the maximal energy $11.4 \leq E < 11.6$ eV (Table I). Here again a molecular state is involved since otherwise minimum energy for ionization of NO should be $D(N_2) + I.P.(NO) = 9.76 + 9.24 = 19$ eV.

The excitation curves in the reaction with $C_2H_2$, cyclo-$C_3H_6$ and NO are in Fig.7*. The curves are marked by a very sharp peak at the energy of about 12.6 eV. This peak is with certainty not experimentally induced. Curve no.2 closely resembles the total efficiency curves given by Lichten and Olmsted, et al.8,15 (Figs.8,9). It characterizes the new high-lying excited state. This state is able to ionize $C_2H_2$ as well as cyclo-$C_3H_6$ and NO. Therefore, the sharp peak appears on all three curves.

The hump at 15 eV belongs to lower lying state (or groups of states) whose released energy must be $10.2 \leq E < 11.4$ eV, as it is able to ionize cyclo-$C_3H_6$ and NO but not $C_2H_2$. Separation of the efficiency curves is therefore possible according to Fig.10.

*It was verified using the apparatus with mass analysis of product ions that the associative ionization (formation of $N_2NO^+$) contributes to the total ion production only negligibly. The ratio of NO$^+$ to $N_2NO^+$ ion currents in the $N_2^+$ - NO reaction is about 10.
The increasing proportion of the lower excited states, as revealed from the change in shape of the excitation functions in ionization of cyclo-C$_3$H$_6$ and NO, can be explained by the combined effect of two factors:

1) Minimally two states are active in ionization of cyclo-C$_3$H$_6$, a$_1$$\Gamma$$^-$ and $^1\Delta_u$, whereas for ionization of NO, molecules in the a$_1$$\Pi_g$ can participate in addition (Fig. 11).

2) Because the potential energy curves for $^1\Delta_u$, a$_1$$\Gamma$$^-$ and a$_1$$\Pi_g$ states have greater equilibrium nuclear separation than the N$_2$ ground state, a number of vibrational levels are populated in excitation, according to Fig. 13. Only the higher lying levels have enough energy to ionize cyclo-C$_3$H$_6$, but NO can be ionized also by molecules in states with lower vibrational quantum numbers. Therefore more molecules are active in ionization of NO than in ionization of cyclo-C$_3$H$_6$. To estimate the variation in the number of active excited molecules the relative population of vibrational states should be considered. Theoretical data are available for the Franck-Condon factors of the a$_1$$\Pi_g$ state only and are presented in Fig. 11b. Despite the fact that enough energy is available in the $v > 8$ vibrational level of this state for ionization of cyclo-C$_3$H$_6$, the number of excited molecules is small due to the small F-Č factor, and the a$_1$$\Pi_g$ state might contribute mostly only to the ionization of NO. Similar consideration applies also for the other states (Fig. 11).
The sharpness of the peak at 12.6 eV is very striking and its occurrence on the efficiency curves of molecular states is unique \*\*\*. The proposed explanation is the following:

The high-lying state is formed in two possible ways. Channel 1 is a resonance capture of an exciting electron by the target \(N_2\) molecule and the decomposition of the unstable \(N_2^{*-}\) ion according to (5):

\*\* A relatively sharp peak appears on the curve for inelastic energy losses in impact with slow electrons, given by Schulz\(^{19}\) (Fig.12). He ascribed it to the excitation of the \(C^3\Pi_u\) state and pointed out that the corresponding excitation function peaks at less than 0.8 eV above threshold.

Care must be taken, however, in comparing the two peaks for these reasons:

1) The process taking place in the region 11 - 12 eV on the Schulz's energy losses curve is the formation not only of the long-lived but also of the short-lived excited states, i.e., the \(C^3\Pi_u\) state. Accidentally, the first process heavily predominates in the case of \(N_2\).

2) The peaks appear on two different curves and their shape is determined by entirely different factors. Whereas on the energy losses curve the principal factor is the relative position of the potential energy curves of the ground and excited states, on the excitation function it is the change of the cross section with the energy of exciting electrons.

\*\* Sharp \# isolated peaks have been discovered recently in electron transmission measurement in \(N_2\) by Heideman, Kuyatt and Chamberlain (Dr. Kuyatt, private communication).
\[ \begin{align*} 
N_2(\frac{1g}{1g}) + e &= N_2^{-*}(\ ? \ ) \rightarrow N_2^*(-\ ? ) + e. 
\end{align*} \]

The state of the resulting \( N_2^- \) is difficult to describe. In the region of the excitation energy of about 11.0 - 12 eV are found the excited states \( C^3\Sigma_u^+, E^3\Pi_g \) and \( 5\Pi \), and perhaps vibrationally excited states \( a^1\Pi_g \), \( a^1\Sigma_u^- \) and \( 1\Lambda_u \). The \( C^3\Pi_u \) and \( E^3\Pi_g \) probably have too short a lifetime since the first decays to the \( E^3\Pi_g \) and the second to the \( A^3\Sigma_u^+ \) states (second positive system, \( \gamma \) bands). The difference in the shape of the efficiency curves No. 1, 2, and 3 proves conclusively enough that the last three states need not to be considered. The state in question must be a long-lived state, singlet or triplet, because the quintet state cannot be formed in a single transition and, when formed by some other process, it cannot react with \( C_2\text{H}_2 \) or other molecules in the singlet state because the spin is not conserved in the reaction

\[ N_2^* (\ ? \ ) + C_2\text{H}_2(\ ? ) = N_2(\frac{1g}{1g}) + C_2\text{H}_2^+(\ ? ) + e. \]

It might be a \( \frac{1g}{1g} \) state, dissociating to \( N(2\text{D}) + N(2\text{D}) \). Its transitions to all lower lying known states are optically forbidden and it should be long-lived with respect to dipole moment transitions.*

Channel 2 is probably a direct excitation of the \( \frac{1g}{1g} \) state involving all cascade processes from higher lying allowed states. The excitation function belonging to this channel is marked by a peak at the energy of about 24.5 eV (Fig. 7).

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* Olmsted, et al., suggested\textsuperscript{15} that the state is one of the \( E \) triplet states.
Carbon Monoxide

According to Table I there should be a long-lived state which makes available upon deexcitation an energy \( 10.2 < E < 11.4 \) eV. Moreover, as the efficiency curves in the reaction with NO and cyclo-C\(_3\)H\(_6\) (Fig. 13) are quite different, very probably two long-lived states are excited. The lower lying state, responsible for the ionization of NO, has the threshold energy 9.8 eV and is marked by a broad peak at about 15.0 eV on the excitation function. The energy of the second, higher lying state, which ionizes cyclo-C\(_3\)H\(_6\), must be \( E > 10.2 \) eV. The states reported in the literature are the \( a^3\Pi \) state, with the energy 6.2 eV\(^8\), and the \( b^3\gamma^*\) state, found recently by Olmsted, et al.\(^{15}\), from the break on the secondary electrons efficiency curve. It should lie at 10.5 eV and can ionize cyclo-C\(_3\)H\(_6\) and NO. It is identical with the higher state reported here. The lower lying state might well be responsible for the rise on Olmsted's curve at the energy of about 10 eV and for the flattening at the energy 13 eV (Fig. 14).

Oxygen

According to previous results\(^{21}\) molecular oxygen should have a long-lived excited state yielding in collision an energy \( 10.2 < E < 11.4 \) eV (Table I.). It is in accordance with Lichten's finding of a metastable state \( 5\Pi \) with an energy of about 12 eV and with a lifetime minimally \( 10^{-3} \) sec. (see \(^{22}\)).

In the apparatus presently used the currents were too small to allow for more detailed investigation.
Cross Sections

The density of ions formed in the collision region is given by

\[ n^+ = n^*_{\text{DM}} l_i \sigma_i \]

where \( n^* \) is the density of excited molecules in the collision region, \( n^*_{\text{DM}} \) is the density of detector molecules, \( l_i \) is the ionization path and \( \sigma_i \) is the Penning ionization cross section. Due to finite lifetime the number of excited molecules diminishes during the passage to the collision region according to

\[ n^*_{t} = n^*_{o} e^{-\frac{t}{\tau}}. \]  \hspace{1cm} (6)

Here \( n^*_{t} \) is the density of excited molecules after a travel time \( t \), \( n^*_{o} \) is the density at \( t = 0 \), and \( \tau \) is the mean lifetime of excited molecules. Hence

\[ n^+ = \alpha n^*_{o} l_i n^*_{\text{DM}} \sigma_i e^{-\frac{t}{\tau}}, \]  \hspace{1cm} (7)

where \( \alpha \) is a correction coefficient for the decrease in the number of excited molecules reaching the collision region due to geometrical factors.

The density of excited molecules at the point of their formation is given by

\[ n^*_{o} = n^*_{e} l_e n^*_{\text{Me}} \sigma_e, \]  \hspace{1cm} (8)

where \( n^*_{e} \) is the density of exciting electrons, \( l_e \) is the excitation path, \( n^*_{\text{Me}} \) is the density of molecules to be excited and \( \sigma_e \) is the excitation cross section. For \( n^+ \) one thus obtains
\[ n^+ = \alpha n_e l_{11} n_n \sigma_i \sigma_e \exp \left( \frac{-t}{\tau} \right). \]  

(9)

A similar expression holds for the Penning ionization with noble gas metastables, e.g., for argon,

\[ n^+_{Ar} = \alpha n_e l_{11} n_n \frac{\sigma_e \sigma_i}{\sigma_i} \exp \left( \frac{-t_{Ar}}{\tau_{Ar}} \right). \]  

(10)

In (10) \( t_{Ar}/\tau_{Ar} \) is the \( Ar^* \) travel time or mean lifetime respectively and \( (\sigma_e \sigma_i)_{Ar} \) is the product of cross sections related to \( Ar \).

It is useful to compare the two ion densities. Their ratio is

\[ \frac{n^+}{n^+_{Ar}} = \frac{n_M \sigma e \sigma_i}{n_M \sigma e \sigma_i} \exp \left( \frac{-t_{Ar}}{\tau_{Ar}} \right). \]

If the currents are measured under the condition that \( n_M = n_{Ar} \), the equation becomes

\[ \frac{n^+}{n^+_{Ar}} = \frac{\sigma e \sigma_i}{(\sigma e \sigma_i)_{Ar}} \exp \left( \frac{-t_{Ar}}{\tau_{Ar}} \right). \]

When more than one state is active, the \( \sigma_e, \sigma_i \) and \( \tau \) are only effective phenomenological values.

Unfortunately not enough is known about \( \sigma_e, \sigma_i \) and \( \tau \), and the present apparatus does not allow for their measurement. The \( \frac{n^+}{n^+_{Ar}} \) values for the ionization of \( NO \) by \( H_2^* \), \( CO^* \) and \( N_2^* \) and for the ionization of \( C_2H_2 \) by \( N_2^* \) are in the Table II.
Only in the case of reaction with \( \text{C}_2\text{H}_2 \) is a very rough estimate of the lower value of \( \sigma_e \) possible. This is because the high-lying new state of \( \text{N}_2^* \) (\( E \approx 11.4 \text{ eV} \)) is probably long-lived enough so that \( \tau > t \) (see 15). Taking \( \sigma_e \) and \( \sigma_i \) for argon as \( 10^{-18} \) and \( 10^{-15} \text{ cm}^2 \) respectively the product \( (\sigma_e\sigma_i)_{\text{Ar}} \) then equals \( 10^{-33} \text{ cm}^2 \). Supposing that \( \sigma_i \) is of the order of \( 10^{-15} \text{ cm}^2 \), the lower limit of the excitation cross section for the new state of \( \text{N}_2 \) is probably of the order of \( 10^{-20} \text{ cm}^2 \).

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

1) Schematic diagram of the arrangement. Symbols are explained in the text.

2) Excitation functions for electron impact excitation of metastable levels of noble gas atoms: Curve 1, He; curve 2, Ne; and curve 3, Ar. Detector molecule: $\text{C}_2\text{H}_2$.

3) a) Excitation function for electron impact excitation of metastable Ar atoms as given by Olmsted, et al.$^{15}$

b) Excitation function for electron impact excitation of metastable Ne and He atoms given by Olmsted, et al.$^{15}$, and Dorrrestein$^6$ (He).

4) Dependence of the positive ion current on the current of exciting electrons. Excited molecules, $\text{N}_2$; detector gas, $\text{C}_2\text{H}_2$. The peak value of the positive current is measured (electron energy 12.6 eV).

5) a) Dependence of the positive ion current on the density of the excited molecules in the source region. Pressure of the detector molecules is held constant. The linear relation between concentration of gases in the source and collision regions and the ionization gauge readings was checked.

b) Dependence of the positive ion current on the concentration of the detector molecules in the collision region at constant pressure of the excited molecules in the source. The positive ion current decreases at pressure greater than about $1.10^{-5}$ mm Hg because of deexcitation and scattering of excited
molecules outside the collision region.

6) Excitation functions for long-lived excited \( \text{H}_2 \). The lower energy scale is calibrated by reference to \( \text{Ar}^* \) efficiency curve. Detector molecules: curve 1, NO; curve 2, \( \text{C}_2\text{H}_2 \).

7) Excitation functions for long-lived excited states of \( \text{N}_2 \). Electron energy is uncorrected.

8) Total excitation function of \( \text{N}_2^* \) given by Lichten\(^8\).

9) Total excitation function of \( \text{N}_2^* \) given by Olmsted, et al\(^15\).

10) Tentative decomposition of the efficiency curve of \( \text{N}_2^* \), detected by ionization of NO, into individual excitation functions. Curve 1, original efficiency curve; curve 2, excitation function for the \( \text{N}_2 \) excited state with the energy \( 10.2 \leq E \leq 11.4 \text{ eV} \); curve 3, excitation function for the high-lying state \( (E \simeq 11.4 \text{ eV}) \).

11) a) Potential energy curves of the \( ^1\Pi_g \), \( ^1\Delta_u \), and \( ^1\Sigma_u^- \) states of \( \text{N}_2 \). The \( ^1\Pi_g \) curve is drawn using the calculated data\(^18\).

b) Horizontal lines: The calculated Franck-Condon factors of the vibrational levels of the \( ^1\Pi_g \) state\(^18\). Curves 1, 2, and 3: approximate envelopes of the Franck-Condon factors as determined by the reflection of the \( \psi^2 \) function of the ground state on the potential energy curves.

12) Energy loss curve of slow electrons in \( \text{N}_2 \) determined by the trap current method\(^19\).
13) Excitation functions for long-lived excited CO. Detector molecule: curve 1, NO; curve 2, cyclo-C$_{3}$H$_{6}$. Curve 3, calibration of the energy scale with Ar$^*$. Curve 2b, positive ion current resulting from subtraction of the current due to the emission of secondary electrons from the collector grid.

14) Total efficiency curve of CO$^*$ given by Olmsted, et al.\textsuperscript{15}
REFERENCES

13) Čermák V.: This report, part II.
21) Čermák V.: Presented at JILA colloquium, October 1964
TABLE I

Ionization Caused by Long-Lived Excited Molecular States

+ ionization occurs,  - no ionization detected

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<thead>
<tr>
<th>Excited molecule</th>
<th>NO</th>
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TABLE II

Ratio of the ion currents in Penning ionization of selected detector molecules by excited long-lived molecules $X^*$ and by argon metastables.

<table>
<thead>
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<th>Electron energy, eV</th>
<th>Detector molecules</th>
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Figure 2
Figure 7
Figure 12
PART II
ON THE EVIDENCE OF THE N₂NO⁺ ION

V. Čermák

Recent investigations \(^1\textsuperscript{–}^9\) showed quite clearly that when mixtures of gases are exposed to exciting radiation (electrons, photons), a considerable amount of ions can be formed by associative ionization (chemi-ionization), i.e., by the reaction

\[ X^* + Y \rightarrow XY^+ + e \ . \quad (1) \]

The symbol \(X^*\) denotes atoms or molecules in an excited state, while \(Y\) denotes atoms or molecules. A number of unexpected ions may be formed in this way, e.g., \(\text{ArHg}^+, \text{HeLi}^+, \text{N}_2\text{Cs}^+, \text{and N}_4^+\).

It was interesting to test whether the ion \(\text{N}_2\text{NO}^+\) can be formed by a reaction of the type (1):

\[ \text{N}_2^* + \text{NO} \rightarrow \text{N}_2\text{NO}^+ + e \ . \quad (2) \]

The binding energy of the \(\text{N}_2\text{NO}^+\) was thought not to be prohibitively small.

To verify the idea, a mass spectrometer with a modified ion source was used (see Fig. 1). In this arrangement only long-lived excited particles can react (\(\tau \geq 10^{-5}\) sec). Only a brief description of its function is given here, since it was presented in full elsewhere \(^1\).
Excited $N_2$ molecules are produced by electron impact in the region A. Charged particles are prevented from entering the collision region B by suitable electric fields. The NO molecules were introduced in the region B in the form of a molecular jet from the side tube $T_M$. Extracted ions were mass analyzed by means of a Nier-type mass spectrometer. Pressure in the collision region was about $10^{-4}$ mm Hg.

The results are shown in Figs. 2-4; $N_2NO^+$ ions were indeed found. The linear dependence of the $N_2NO^+$ ion current on the current of exciting electrons and the dependence on the pressure of both gases assured that only single collisions were involved. A departure from linearity in the $i_{N_2NO^+} = f(p_{NO})$ and $i_{N_2NO^+} = f(p_{N_2})$ plots (Fig. 2) at higher pressure of NO or $N_2$ can be explained as the inactivation of $N_2$ molecules caused by NO escaping from the collision region B, or $N_2$ escaping from the collision region A.

The excitation function of $N_2^*$ (dependence of the $N_2NO^+$ current on the electron energy)--Fig. 3--has a form resembling that for optically forbidden transitions, in accordance with the fact that in the present arrangement only long-lived $N_2^*$ molecules are active in the reaction. The curve closely resembles that for ionization of NO by excited long-lived molecules of $N_2$. The energy of the excited reactive $N_2^*$ cannot be evaluated from the onset of the function, since the current of $N_2NO^+$ was very small. Its energy must necessarily be lower than the I.P. of NO. The reactive state or states are probably the long-lived $a^1\pi$, $a'1\Sigma_u^-$, or $1\Delta_u$ states.

The lower limit of the dissociation energy of $N_2NO^+$ will be readily obtainable once the A.P. (appearance potential) of $N_2NO^+$ (and the energy of
the N₂ state) is known. Supposing that N₂NO⁺ dissociates according to (3),

\[ N₂NO⁺ \rightarrow N₂ + NO⁺ , \]  

then \( D(N₂NO⁺) \) is simply

\[ D(N₂NO⁺) \geq I.P.(NO) - A.P.(N₂NO⁺) . \]  

The idea that the N₂NO⁺ ion has significance for upper atmosphere chemistry is not excluded. This ion has not yet been found in rocket experiments, but this might be partly because the sensitivity and resolving power of mass spectrometers used have been low and partly because nobody has looked for it.

A rough estimate of N₂NO⁺ ion concentration in that region of the upper atmosphere where NO is relatively abundant may be made as follows: The kinetic equation is

\[ \frac{d[N₂NO⁺]}{dt} = \frac{k_r}{k_r} [N₂*][NO] - k_n [N₂NO⁺] \cdot n_e \]  

where \( k_r \) is the reaction constant, \( k_n \) is the recombination constant, and \( n_e \) is the density of electrons.

Under steady state

\[ \frac{d[N₂NO⁺]}{dt} = 0 ; \]

therefore,

\[ [N₂NO⁺] = \frac{k_r [N₂*][NO]}{k_n \cdot n_e} \]
Taking \( k_r = 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{sec}^{-1} \), \([\text{NO}] = 10^7 \text{ molec cm}^{-3}\),

\([n_e] = 10^5 \text{ cm}^{-3} \), and \( k_n = 10^{-6} \text{ cm}^{-3} \text{ sec}^{-1} \),

one obtains an estimate of the maximum concentration of \( N_2\text{NO}^+ \) at the height of about 120 km:

\[
[N_2\text{NO}^+] = \frac{10^{-10} \cdot [N_2^*] \cdot 10^7}{10^{-6} \cdot 10^5} = 10^{-2} [N_2^*].
\]

This result suggests that associative ionization might be a suitable means for detecting the concentration of excited particles in the upper atmosphere. While the reaction (2) with \( \text{NO} \) originating in the upper atmosphere leads to the \( N_2\text{NO}^+ \) ion concentration which is probably unmeasurably small, it is quite certain that the same reaction with \( \text{NO} \) introduced artificially into the source of rocket-born mass spectrometer would give a current of \( N_2\text{NO}^+ \) accessible to the measurement. A concentration of \( \text{NO} \) in the source of \( 10^{13} \) molec/cc \((p \sim 3.10^{-4} \text{ mm Hg}) \) would increase the concentration, so that \( [N_2\text{NO}^+] \sim 10^4 [N_2^*] \).

Similarly, another reaction can be used for the \( N_2^* \) detection, e.g.:

\[
N_2^* + M = N_2M^+ + e^-,
\]

where \( M \) is an alkali metal or mercury atom. For this reaction a cross section of the order of \( 10^{-15} \text{ cm}^2 \) can be expected. Whereas the reaction with alkali metals is suitable for the measurement of the concentration of excited \( N_2 \) molecules, including the \( A^3\Sigma_u^+ \) state, the reaction with either Hg or NO yields the concentration of excited \( N_2 \) molecules in
higher lying states. The relative proportion of excited states undergoing associative ionization can be investigated by closer study of the shapes of excitation functions for the reactions in question.

Conclusion

It is quite clear that the significance of associative ionization for atmospheric chemistry is straightforward although not yet recognized. This paper showed that associative ionization certainly should be considered as one of the means for destruction of metastable particles in the upper atmosphere. It might contribute also to the ionization in the shock-wave produced in re-entry of space vehicles or space bodies in the denser atmosphere layers.

Acknowledgements

I wish to thank Mrs. V. Dubová, Institute of Physical Chemistry, Prague, for the mass spectrometric measurement, and L. Branscomb, JILA, for the remarks on shock-wave ionization.
References

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Figure Captions

1) Schematic Diagram of the Ion Source

T_a multiple channel tube for introducing particles to be excited
A excitation region
E electron beam
G, P_1, P_2 grid and deflecting plates
B collision region
T_m multiple channel tube for introducing molecules
EP extracting plates
FP focusing plates

2) Dependence of the N_2NO^+ Ion Current on the Pressure of NO (curve 1) and N_2 (curve 2) in the Reservoirs. (Linear relation between this pressure and the density of N_2 in the region A and of NO in the region B holds.)

3) N_2NO^+ Ion Efficiency Curve.