Luminescence of Diatomic Molecules
II. Energy Dependence of Collisional Deactivation Cross Sections
F. J. COMES and F. SPEIER *
Institut für Physikalische Chemie der Universität Bonn

Introduction

One spectroscopic means for analysis of a gaseous sample is to measure its emission spectrum. Luminescence spectra give detailed information about the state of the molecules in question. The measurement of luminescence allows conclusions to be drawn about other competing processes, e.g., collisional deactivation, if the remaining experimental parameters such as time and gas pressure are considered. This procedure has been described in paper I for excited molecular ions. In this earlier publication molecular ions at room temperature having a thermal velocity distribution were treated. The measured cross sections for collisional deactivation are thus valid for this mean energy only. In general the method provides information about a large number of molecular states. This makes it possible to measure the influence of the excitation energy of a molecule on the ongoing collisional processes. Also the influence of the translational energy in these collisions can be measured. This is comparatively easy in the case of ionic collision partners. Only a relatively simple additional experimental setup as compared to that described in paper I is required. A variable electric field of defined geometry is introduced inside the collision chamber so that the ions can be accelerated after their formation. The ions will not have a uniform energy at the moment of collision with neutral particles but mathematically a correlation between the mean energy of the colliding ions and their corresponding cross sections can be achieved. This method is especially interesting for two reasons. First, collisional deactivation of even short-lived excited ions \( t \approx 10^{-8} \text{ sec} \) can be investigated, and second, it allows experimental investigations in the energy region between the thermal energy and 1 eV. This region is of importance for upper atmosphere problems and interesting theoretical considerations are also involved. Beam experiments usually are restricted to ionic energies above 1 eV and to ions in their ground state.

In the past many experiments were undertaken to measure the energy dependence of ion-neutral collisions. Charge transfer and ion-molecule reactions were emphasized. For both processes theoretical models were developed which are, however, restricted to atoms in the case of charge transfer. GIOUMOUSIS and STEVENSON applying Langevin’s calculations to describe ion-molecule reactions predict that the product of cross section and particle velocity for such a reaction is constant. The quantum state of the ion is not taken into account; only the polarisability of the neutral collision partner is considered. Many experimental attempts were made to check this theory.

The way to determine the energy dependence of such cross sections, however, differs in a luminescence experiment from other experimental methods. The result of a collision process, namely the product...
ion, is not observed, but the influence of the collision upon the concentration of the primary ion is measured. This makes an additional statement necessary about the type of process occurring during the collision.

In paper I the mechanism of the collision process has been already discussed. We concluded from the data that the deactivation originates neither in a charge transfer nor in an ion-molecule reaction, but in an internal energy transfer. Electronic energy of the molecular ion is transferred predominantly into vibrational energy through radiationless transitions. Though processes of this kind are sometimes discussed in the literature no treatment of their energy dependence has yet been given.

**Experimental**

The apparatus has already been described in paper I. Monochromatic light of wavelength 584 Å from a He resonance lamp enters through a UV transmitting collodium film into the collision chamber. There it ionizes and excites the different diatomic gases. Their luminescence is observed in a direction perpendicular to the primary light beam with a photomultiplier and a monochromator. In addition to the experimental setup described in paper I two condensor plates are installed in the collision chamber which produce a homogeneous electric field when a voltage \( U \) is applied. The field is perpendicular to the directions of both the primary light and that of observation. The field strength is continuously variable between 0 and 120 V/cm. The measurements were carried out at pressures of 0.06 and 0.1 Torr. At these pressures the range of the accelerated ions is even in the most unfavourable case not larger than 1/3 of the width of the observed region.

The question of whether the electric field produces polarization or anisotropy of the fluorescence also arises. Under the experimental conditions such an effect would have an unknown influence on the light intensity ratios obtained with and without the field applied. As a test the measurements were repeated with the grating monochromator turned through 90° about its axis. They were repeated again with the electric field turned through 90° so that it was parallel to the direction of the light entering the monochromator. For this purpose one of the condensor plates was replaced by a grid of high optical transmittance. All three measurements led to identical results.

**Data Processing**

Accordinig to Fig. 1 the excited molecular ions are produced in the homogeneous field of a plate condensor. They are accelerated from their forma-
the excited ion as compared to the time between collisions. For energies greater than 0.1 eV, $\Phi(U)$ should remain practically constant. Actually a different curve for $\Phi(U)$ was measured as Fig. 2 shows qualitatively. It follows that the deactivation cross section $\sigma$ cannot be proportional to the inverse ionic velocity.

Instead $\sigma$ decreases more slowly with increasing $v$.

The quantitative dependence of the deactivation cross section $\sigma = \pi d^2$ on the kinetic energy $E$ is calculated from the measured luminescence intensity $\Phi(U)$, the applied voltage $U$ and the gas pressure $p_0$. The various steps of the calculation are summarized in Fig. 3 and are as follows.

The excited ions are accelerated in the electric field. The deactivation cross section $\sigma(E)$ changes with increasing energy as has been discussed above. In addition it has to be considered that the motion of the ions is also influenced by collisions which do not lead to deactivation. These are expected to be elastic. Their probability is calculated from the gas kinetic cross section $\sigma_g$ which is assumed for our purpose to be independent of the energy $E$. These assumptions are acceptable within the limits of error obtained as will be shown later. As explained in paper I the mean lifetime $t_d$ with respect to collisional deactivation is obtained from measurements at different gas pressures $p$, if the natural lifetime $\tau$ of the species is known. At a pressure $p_0$ and for $U = 0$ this time is $t_{d0}$. We calculate $t_d$ for one specific ap-

![Fig. 2. Schematic diagram of fluorescence intensity $\Phi$ versus voltage $U$ applied across the reaction chamber. (a) according to $\sigma \sim E^{-0.5}$ dependence; (b) measured for short natural lifetimes of the excited particles; (c) measured for long natural lifetimes of the excited particles.](image)

![Fig. 3. Flow diagram for calculations.](image)
plied voltage $U$ from the measured intensity ratio $\Phi(U)/\Phi(0)$. Then the average number of elastic collisions which the ions undergo within $t_d$ is computed. The ion energy $E$ or the velocity $v$ is calculated by vector addition of the thermal velocity and the velocity due to the acceleration in the electric field, allowing for the above mentioned elastic collisions, which occur with a cross section $\sigma_\Omega$. $E$ can either be described as a function $f(t)$ or $g(s)$ where $t$ and $s$ are the time and the distance travelled since ionization, respectively. Inserting $t_d$ into $E = f(t)$ leads to $E_d$, the mean energy at the moment of the deactivating collision. Correspondingly $s_d$ is obtained using $g(s)$. $s_d$ is the mean path length to the deactivating collision.

The deactivation cross section $\sigma_d$ of a particle with mean energy $E_d$ remains to be calculated. We start by assuming the energy dependence of $\sigma(E)$. It seems reasonable to try

$$\sigma \sim E^{-\beta}. \quad (2)$$

For the value of $\alpha'$ we expect $0 \leq \alpha' \leq 1$. In the zero order approximation we start with $\alpha' = 0$ for simplicity. The function $E = g(s)$ can be approximated very well by

$$E \sim s^\beta. \quad (3)$$

The value of $\eta$ is chosen to produce maximum agreement between Eq. (3) and $E = g(s)$ within the range of $s$ values in question ($\eta \approx 0.8$). (2) and (3) lead to

$$\sigma = D s^{-\beta} \quad (4)$$

with $\beta = \alpha' \eta$. $D$ still has to be calculated. Taking the decrease in the number of excited ions along the coordinate $s$ due to deactivating collisions into account one can from Eq. (4) calculate the probability $w(s_d) = w(D)$ as a function of the unknown parameter $D$. $w(s_d)$ is the probability for deactivation within a pathlength $s_d$. From $w(s_d)$ an expression for the mean value of $s_d$ is obtained which still contains the unknown parameter $D$. Comparison of this value $s_d(D)$ to the above-mentioned experimental value for $s_d$ leads to a numerical value for $D$. $\sigma_d$ can now be calculated from

$$\sigma_d = D s_d \quad (5)$$

since $D$, $s_d$ and $\beta$ are known numbers.

The values of $E_d$ and $\sigma_d$ calculated as described above represent one point in a $\sigma - E$ diagram. This point corresponds to a certain voltage $U$ applied to the condenser plates in the collision chamber. The same method of calculation employed for other values of $U$ results in further pairs of $\sigma - E$ values. All these points together produce a plot of $\sigma$ as a function of $E$, which turns out to be a straight line on a $\lg \sigma - \lg E$ scale. In the first order approximation the deactivation cross section is given by

$$\sigma' = \sigma_0 E^{-\alpha}. \quad (6)$$

$\sigma_0$ is the cross section at unit energy.

The fact that the values of $\alpha$ in Eq. (6) and (7) are identical and that only $\sigma_0$ and $\sigma_0'$ differ from one another is an unexpected result which may need some explanation. The energy scale is determined by the measured data, together with the chosen values for the electric field strength, the gas pressure $p_0$, and the choice of $\sigma_\Omega$. From this the correlation between electric field strength and collisional energy $E_d$ is unique and does not depend upon the value of $\alpha'$. The remaining steps of the calculation are directed towards an extraction of the deactivation cross section from the experimental data for each voltage applied. The choice of $\alpha'$ only determines to what extent a particle of momentary energy $E$ out of the total energy distribution contributes to the deactivation cross section. For example large $\alpha'$ values increase the influence of ions with small energy upon the calculation of $\sigma_d$. The opposite is true for small values of $\alpha'$. The exponent $\alpha'$ determines a factor in $\sigma_d$ which is constant for all electric field strengths provided that the energy is large compared to thermal energy. This only leads to a parallel shift on a $\lg \sigma - \lg E$ diagram. Change of $\sigma_\Omega$, however, influences both $\alpha$ and $\sigma_0$. Only if $\alpha = 1/2$ the final result is independent of the choice of $\sigma_\Omega$. In this case the points on a $\lg \sigma - \lg E$ diagram move exactly along a straight line with slope 1/2. If $\alpha$ is actually close to 1/2, as will be shown in the following section, the choice of $\sigma_\Omega$ is not very critical for calculation of the energy dependence of the cross section. As an example we carried out alternative calculations with $\sigma_\Omega = 43.1$ Å² ($N_2$) and $\sigma_\Omega = 0$. Though the energies $E_d$ differed by about
The cross section \( \sigma(E_{th}) \) of the mean energy at a thermal distribution with \( E_{th} = 0.0379 \text{ eV} \) at 20°C has to be calculated separately. In paper I we have measured the mean cross section for a thermal energy distribution \( \sigma(E_{th}) \). Because of the energy dependence of \( \sigma \), however, in general

\[
\sigma(E_{th}) = \sigma(E_{th}) \left( \frac{2}{\sqrt{\pi}} \right) I(1.5 + \alpha)
\]

Introduction of the Maxwell distribution leads to

\[
\sigma(E_{th}) = \sigma(E_{th}) \left( \frac{2}{\sqrt{\pi}} \right) I(1.5 + \alpha)
\]

The factor \( \left( \frac{2}{\sqrt{\pi}} \right) I(1.5 + \alpha) \) is equal to 1 for \( \alpha = 0 \), i.e., both cross sections are equal if \( \sigma \) does not depend on energy. The factor is between 0.92 and 0.93, however, for \( 0.25 \leq \alpha \leq 0.5 \).

**Results and Discussion**

The dependence of the deactivation cross section on the kinetic energy of the ions was measured for the following ionic species and their excited states:

- \( \text{CO}^+ \) \( A^2II, \quad v' = 0, 1, 2, 4, 5 \)
- \( \text{B}^2\Sigma^+ \), \( v' = 0, 1 \)
- \( \text{N}_2^+ \) \( B^2\Sigma_u^+, \quad v' = 0 \)
- \( \text{O}_2^+ \) \( B^4\Sigma_g^-, \quad v' = 1, 2 \).

In all cases the ions were colliding with their parent molecules which were in the ground state. The cross sections were calculated from luminescence measurements corresponding to the following transitions:

- \( \text{CO}^+ \) \( A \rightarrow X \)
  - \( 0 \rightarrow 1 \)
  - \( 1 \rightarrow 0 \)
  - \( 2 \rightarrow 0 \)
  - \( 4 \rightarrow 0 \)
  - \( 5 \rightarrow 0 \)

- \( \text{N}_2^+ \) \( B \rightarrow X \)
  - \( 0 \rightarrow 0 \)
  - \( 1 \rightarrow 0 \)
  - \( 2 \rightarrow 1 \)

- \( \text{O}_2^+ \) \( b \rightarrow a \)
  - \( 0 \rightarrow 0 \)

Measurements were carried out for kinetic energies between thermal and 6 eV maximum. All energies \( E \) are measured with respect to the center of mass and using reduced masses.

In all cases a linear correspondence between the logarithm of the cross section \( \sigma = \pi d^2 \) and the logarithm of the kinetic energy \( E \) was found. \( d \) is the sum of the radii of the two colliding particles. Possible narrow band structures in the representation of the cross section would hardly be detected by the method, due to the averaging process.

Figure 4 shows a typical result. The deactivation cross section is plotted as a function of kinetic energy for the collision of a \( \text{CO}^+ \) \( A^2II \) ion. The transition \( A^2II v' = 2 \rightarrow X^2\Sigma^+ v'' = 0 \) was measured.

![Figure 4](image)

The cross section was expressed using two different scales in order to check the energy dependence. The lower curve (a) shows the values in a \( \lg \sigma - \lg E \) diagram whereas the upper curve (b) is a \( \sqrt{\sigma} - \lg E \) plot. In the double logarithmic representation the points lie on a straight line between thermal energy and 3 eV within experimental error. Thus the energy dependence can be represented as

\[
\sigma = \sigma_0 E^{-\alpha} \tag{7}
\]

which has been already discussed in the preceding section. For this collision \( \alpha \) is found to be 0.36 ± 0.02. A dependence of the cross section on energy such as

\[
\sqrt{\sigma} = k_1 - k_2 \ln \sqrt{E} \tag{8}
\]

is, however, excluded. This is clearly demonstrated by curve (b) of Figure 4. The deviation of the experimental points from a straight line are far beyond experimental error. Equation (9) has been given by Rapp and Francis for charge exchange collisions of atomic ions. It was also successfully applied by Hough and Bayes to describe charge exchange collisions of molecules. One should, how-
ever, not expect that Eq. (8) describes correctly the collision processes discussed here, because, as was already pointed out in paper I, charge exchange is only of small importance in this case.

Figures 5 a and b show the degree to which Eq. (7) correctly describes the measured data of all the molecular states examined. Uncertainty due to experimental error is very small below 2 eV. It is comparable in size to the diameter of the dots in Figs. 5 a and b. It is larger in the higher energy region. More important than the experimental error for all points is the systematic error due to approximations during the data processing.

This luminescence intensity which never accounted to more than 10% of the primary luminescence was subtracted from the measured intensity obtained with the He-lamp. The different He- and Ne-lamp intensities were, of course, measured and considered. Due to the small variation of $\Phi(U)$ for $N^+_2B$ and $CO^+ B$ [cf. Fig. 2 (b)], as compared to that in Fig. 2 (c) for $CO^+ A$ and $O^+_2 b$, corrections in $\Phi$ change $\sigma(E)$ much more in case of short-lived ions than in case of long-lived ones. Consequently a possible error in this correction has a more serious effect upon the shortliving ionic states. We therefore conclude that the positive deviation from the linear dependence in a $\lg \sigma - \lg E$ plot as shown by the long-lived molecular ions is correct. The different behaviour of the short-lived states might still be caused by accelerated photoelectrons and thus be erroneous.

Thus far no measurements have been carried out of the energy dependence of deactivation cross sections for excited molecular ions. However such results for collisions of molecular ions in their ground state have been obtained. Paulsen, Mosher, and Dale examined the ion-molecule-reaction

$$O^+ + CO_2 \rightarrow O_2^+ + CO$$  \hspace{1cm} (9)
suits which can be described by Eq. (7). The values of \(a\) inferred from these experiments for the various ion-molecule reactions and charge transfer processes are in the range zero to 1.1. They also confirmed the result of Paulsen, Mocher, and Dale.\(^7\) The collision cross sections lie, with one exception, between 10 and 100 Å\(^2\). They are thus comparable in size to the results of the present experiments. In both cases mentioned above mass spectrometers were employed. Therefore, the product ions and also the reaction paths are known. The energy dependence was not discussed.

Gioumousis and Stevenson\(^4\) calculated, on the basis of the Langevin potential, the energy dependence of the cross section \(\sigma\) for ion-molecule reactions. They find

\[
\sigma = 5.33 \sqrt{\alpha_2} m / \mu E \, \text{Å}^2 \sim E^{-\frac{1}{2}}. \tag{10}
\]

Here \(\alpha_2\) is the polarizability in units of 10\(^{-25}\) cm\(^3\), \(m\) the mass of the ion, and \(\mu\) the reduced mass, respectively. The model does not take into account the molecular properties of the ions. They are regarded as point charges. The neutral collision partner is described by its polarizability in the Coulomb field of the ion. Ion-molecule reactions have been found which follow this theoretical prediction in the low energy region.\(^9\) The measurements are in many cases not exact enough to exclude a deviation of the exponent \(a\) in Eq. (8) by 0.1.

Dunbar\(^10\) has calculated an energy dependence for the reaction of CH\(_4\)\(^+\) with CH\(_4\) at energies up to 1 eV. He finds \(\sigma \sim E^{-0.45}\). He added to the Langevin term in the interaction potential \(V = \alpha^2 \alpha_2 / (2 r^4)\) the potentials

\[
V_{\text{ind}} = 3 a_2^2 h v / (4 \pi r^6) \quad \text{and} \quad V_{\text{dis}} = 3 I_1 I_2 a_1 a_2 / [2 r^6 (I_1 + I_2)]
\]

with \(I_1\) and \(I_2\) being the ionisation potentials and \(a_1\) and \(a_2\) the polarizabilities of the molecule and ion, respectively. \(V_{\text{ind}}\) and \(V_{\text{dis}}\) represent a charge-induced quadrupole moment and the dispersion forces. They result in a slower decrease of \(\sigma\) with \(E\) than is described by \(\sigma \sim E^{-0.5}\). Unfortunately these formulas cannot be applied to interpret the results of this work, because most of the values which have to be inserted into the above equations are unknown for the systems in question. An approximation would not be exact enough. The observed positive deviations of the cross section from the straight lines in Figs. 5 a and b indicate that the interaction potential for small cross sections must increasingly resemble the potential of a hard sphere.

Equation (8) correctly describes the energy dependence of the cross section for most energies and for all excited states of the ions studied. The cross sections for ions at thermal energy \(\sigma_{\text{th}}\) extend from 40 Å\(^2\) to 190 Å\(^2\). Equation (10) predicts values of \(\sigma_{\text{th}}\) for N\(_2\)\(^+\), O\(_2\)\(^+\), and CO\(^+\) colliding with their parent molecules between 110 Å\(^2\) and 120 Å\(^2\). Thus the experimental results deviate considerably in both directions from the theory based on the Langevin potential. Besides the deactivation cross section at a given energy the value of \(a\) is also a characteristic property of the collision. Observed values lie between 0.34 and 0.41 (Table 1). \(a\) only changes by about 20%. It is difficult to imagine an explanation of both the small deviation of \(a\) from 0.5 and the large deviations of \(\sigma_{\text{th}}\) from 115 Å\(^2\) based on Dunbar's considerations alone.

<table>
<thead>
<tr>
<th>(\sigma_{\text{th}} , [\text{Å}^2])</th>
<th>(a)</th>
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<tbody>
<tr>
<td>CO(^+)</td>
<td>(v' = 0)</td>
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<tr>
<td>N(_2)(^+)</td>
<td>(v' = 0)</td>
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<td>CO(^+)</td>
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<td>CO(^+)</td>
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<td>O(_2)(^+)</td>
<td>(v' = 1)</td>
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<tr>
<td>CO(^+)</td>
<td>(v' = 5)</td>
</tr>
<tr>
<td>O(_2)(^+)</td>
<td>(v' = 2)</td>
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The values of \(a\) differ slightly from each other for the various ions and their states. With the exception of the vibrational ground state of CO\(^+\) A, \(a\) does not depend upon the vibrational quantum number of the electronically excited state within experimental error. CO\(^+\) B and O\(_2\)\(^+\) B show the same behaviour. With the exception of CO\(^+\) A \(v' = 0\) the differences in \(a\) could be interpreted as being due to the differences in the electronic states of the ions. A different interpretation, which would include CO\(^+\) A \(v' = 0\) views \(a\) as a function of \(\sigma_{\text{th}}\); \(a\) would decrease with increasing \(\sigma_{\text{th}}\). Upon examination of Table 1 this seems to be a probability which can, however, not be proven exactly by the present results. In order to examine the dependence of \(a\) on specific molecular constants one needs more measurements of different ions and in particular a larger number of measurable excitations of one kind of molecular ion.
Einige Bemerkungen über die Erzeugung von elektromagnetischen Wanderwellen und stehenden Wellen zur induktiven Plasmabeschleunigung

A. MEERT
Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt e.V.
Institut für Energiewandlung und Elektrische Antriebe, Stuttgart

Some Comments on the Generation of Travelling and Standing Electromagnetic Waves for Inductive Plasma Acceleration

Some comments are made for the generation of e.m. travelling and standing waves used for inductive plasma acceleration. Resulting from a simple mathematical formulation the different features lead to a non-conventional method for travelling wave generation, which is compared with the basic method — i.e. the standing wave generation — with regard to Ohmic losses and magnetic energy density.

1. Einleitung


Die Beschleunigung von Plasmen mit Wanderwellenanlagen wird in der Literatur ausführlich behandelt (s. z. B. 1—5). Systeme mit stehenden Wellen zur Plasmabeschleunigung werden im hiesigen Institut untersucht (z. B. 4, 5).


Die bereits angewandten Methoden zur Erzeugung von Wanderwellen mit Phasengeschwindigkeiten von einigen 100 km/sec und Wellenlängen im dm-Bereich bestehen darin, daß man entweder eine Laufzeitkette benutzt (z. B. 6) oder ein Spulensystem, wobei jede einzelne Spule mit einer zu den benachbarten Spulen zeitlich phasenverschobenen Stromversorgung versehen wird (z. B. 7).

Bei Anwendung einer Laufzeitkette muß das Netzwerk mit einem Abschlußwiderstand abgeschlossen werden. Die nicht an das Plasma abgegebene Energie muß durch diesen Widerstand absorbiert werden, um Reflexionen zu vermeiden.

Bei den gepulsten Anlagen wird praktisch die gesamte eingespeiste Energie im Abschlußwiderstand der Kette verbraucht. Der Wirkungsgrad ist somit sehr schlecht. Da sich die energetischen Vorgänge jedoch in sehr kurzen Zeiten (μsec-Bereich) abspielen, sind die erzielten Leistungen so groß, daß immer noch genug Leistung für die Plasmaexperimente übrig bleibt. Bei kontinuierlich arbeitenden Anlagen spielt der Wirkungsgrad jedoch eine wesentliche Rolle, da die kontinuierlich zur Verfügung stehende Leistung aus praktischen Gründen um Zehnerpotenzen kleiner ist als die beim Pulsbetrieb auftretenden Leistungen.

Eine wesentliche Verbesserung dieses Wirkungsgrades kann durch eine Rückkopplung erzielt werden, deren technische Realisierung sich als schwierig und aufwendig erweist (Jülicher Arbeiten, z. B. 8).