Luminescence of Diatomic Molecular Ions

I. Franck-Condon-Factors and Collisional Deactivation

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The ionic species N_2^+ B, CO^+ A, CO^+ B, and O_2^+ b have been produced by irradiation with the He I resonance line. Franck-Condon-factors both for excitation and deexcitation have been deduced from the fluorescence of the molecular ions. Most of them agree with calculated values of the Franck-Condon-factors. Measurements at different pressures ranging from 0.005 to 5 Torr lead to the deactivation cross sections for collisions with the parent molecule. N_2^+ B also is deactivated in collisions with O_2. Cross sections vary between 50 Å² and 250 Å² depending upon the ionic species and its vibrational quantum number. The deexcitation is described as a radiationless transition where electronic energy is transfered into vibrational energy.

Introduction

Photoelectron spectroscopy has become a standard method for the determination of unknown states of excited molecular ions. It is also well suited for the evaluation of Franck-Condon-factors (FC-factors) of ionization processes. In most cases the vibrational levels can easily be resolved. Resolution is limited, however, by the thermal motion of the molecules. In comparison to photoelectron spectroscopy there is no such restriction in optical spectroscopy, where ionic species are identified by their fluorescence. Doppler line broadening is only small compared to the difference between two adjacent rotational lines. It is of negligible importance for nearly all investigations. Resolution is generally limited only by the amount of primary light intensity available. Fluorescence spectra permit evaluation of the FC-factors including the electronic transition matrix elements not only for the emission itself, but also for the primary absorption step which led to ionization. Contrary to the above-mentioned photoelectron spectra, optical spectra only inform about fluorescing species.

Molecular fluorescence depends upon the particle's environmental conditions. Electric and magnetic fields cause the Stark- and Zeeman-effect, respectively. Also chemical reactions – generally speaking collisional processes – can change the fluorescence of excited ions. Knowing the natural lifetime of the excited species one can even determine the kinetics of the collisional process which might occur only 10^{-8} s after excitation. The intensity of fluorescence has for that purpose to be measured as a function of gas pressure.

This paper describes measurements of FC-factors for excited CO^+ and N_2^+ molecular ions. Collisional deactivation cross sections are determined for various states of different electronic and vibrational energy of CO^+, N_2^+, and O_2^+. Primary ionization is accomplished by the He I resonance line ($\lambda = 584$ Å $\triangleq 21.21$ eV). A future publication will deal with the dependence of the cross section upon the translational kinetic energy of the ions.

Experimental

Unlike electron impact ionization, photoionization produces only a small number of known electronic states of the molecular ion. That is because photon energy does not have to exceed the required energy needed for the production of the fluorescing state. The He I resonance line produces various known fluorescing ionic states of diatomic molecules. Their photoionization cross section at 21.21 eV is large enough to garantee sufficient ion intensity necessary for the experiment. The He I resonance line can be produced without the need for a monochromator in a microwave discharge. Whereas in the present experiment relatively many photons of 21.21 eV reach the reaction chamber (1.5×10^{12} photons/s), intensity is negligibly low for other emission lines such as the He II resonance line ($\lambda = 304$ Å $\triangleq 40.41$ eV) or further lines of the He Lyman series (537 Å $\geqq \lambda \geqq$ 504 Å). The microwave discharge is operated at 100 W, 2450 mc and at a gas pressure of 1 Torr. Figure 1 shows a block diagram of the apparatus.

Measurements at different gas pressures are needed for the determination of the deactivation cross sections. These measurements in turn need an absorption path which is well defined both in respect to length and pressure. Therefore a window of thin uv-transmitting collodium film separates the light source from the absorption, fluorescence and collisional deactivation cham-

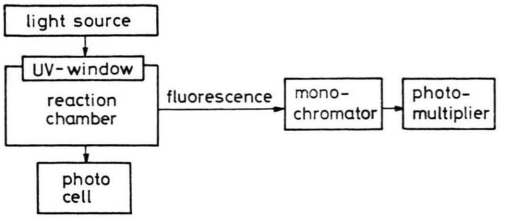

Fig. 1. Block diagram of the apparatus.

ber. The average thickness of the film was found gravimetricly to be 150 Å ± 10 Å. It is supported by a fine nickel mesh of 85% transmittance, which is 5 mm in diameter. There is a differential pumping section between the light source and the film in order to prevent the film from being burned by the discharge, to avoid deposition of impurities on its surface and to reduce resonance absorption of the He I line. Figure 2 shows

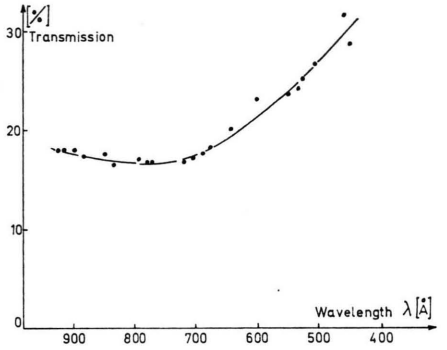

Fig. 2. Transmission of the collodium uv-window as a function of wavelength.

the transmission (%) of the window for uv light between 900 Å and 450 Å. The absorption coefficients coincide with the values of LUKIRSKII, FORMICHEV, and BRYTOW [1] who measured the absorption for smaller wavelengths (Table 1). Our experiment also requires that the film seal off the chamber tightly. At a reaction chamber pressure of 0.1 Torr no more than 10^{12} par-

Table 1. Absorption coefficients μ [cm^{-1}] for collodium (dinitrocellulose) at wavelength λ [Å]. 100 Å $\leqq \lambda \leqq$ 415 Å: LUKIRSKII et al. [1]; 450 Å $\leqq \lambda \leqq$ 900 Å: this work.

λ [Å]	μ [cm^{-1}]	λ [Å]	μ [cm^{-1}]
100	5.0 (+ 4)*	415	8.0 (+ 5)
150	1.1 (+ 5)	450	7.3 (+ 5)
200	2.2 (+ 5)	500	8.1 (+ 5)
250	3.3 (+ 5)	600	1.0 (+ 6)
300	4.8 (+ 5)	700	1.2 (+ 6)
350	6.3 (+ 5)	800	1.3 (+ 6)
400	7.4 (+ 5)	900	1.3 (+ 6)

* $5.0(+4) \equiv 5.0 \cdot 10^4$.

[1] A. P. LUKIRSKII, V. A. FORMICHEV, and I. A. BRYTOV, Opt. Spectr. **20**, 202 [1966].

ticles per second leak through the film into the differential pumping section. The leak rate increases linearly with increasing chamber pressure up to 30 Torr. At about that pressure the film is destroyed. Leakage through the film does not influence the measurements. After about 5 hours of exposure to uv radiation the film becomes increasingly less transmitting. All series of measurements were started with unused films.

A Ni-cathode photo cell at the bottom of the chamber measures the primary radiation intensity when no absorbing gas is present (Fig. 1). The fluorescence which is emitted into the direction of the analysing monochromator passes through a suprasil window and is focussed by a collimating lens system onto the entrance slit of a grating monochromator. Light which is emitted in the opposite direction also contributes to the total measured intensity through reflection at an aluminum coated concave mirror. The monochromator operates at a focal length of 0.5 m with a minimal bandwidth of 1.5 Å. An additional suprasil lens at the monochromator exit focusses the light onto the cathode of a photomultiplier. Depending upon wavelength an EMI 6256SA or EMI 9558A was used. A high signal to noise ratio is achieved by a counting method employing a discriminator stage and a ratemeter with a recorder. The multiplier is cooled to −80 °C in order to reduce noise to 1 − 3 counts per second. A separate vacuum chamber prevents the photomultiplier from frosting.

Measurement and Calibration

Photoionization produces various excited molecular ions in the reaction chamber. Due to their final lifetime, there exists a certain probability that they encounter deactivating collisions with other particles instead of loosing their excitation energy by natural fluorescence. The fluorescence signal is lowered by these deactivating collisions. The fluorescence of different excited states is measured as a function of pressure. According to STERN and VOLMER [2] the inverse fluorescence intensity per unit of absorbed radiation is plotted against pressure, normalized to unity for zero pressure. The presence of a linear dependence indicates the bimolecularity of the deactivating process. The slope equals the product of rate constant and natural lifetime. If the latter is known the rate constant (or cross section) can be calculated. FC-factors are calculated from fluorescence intensity ratios which have been extrapolated to $p = 0$.

The knowledge of the relative wavelength dependence $D(\lambda)$ of the detector system sensitivity is a prerequisite for the determination of relative fluorescence intensities. $D(\lambda)$ includes window transmittance, monochromator effectiveness, and photomultiplier sensitivity. It is only needed for the system as a whole, not for the individual components.

[2] O. STERN and M. VOLMER, Physik. Z. **20**, 183 [1919].

In the visible and near uv region a tungsten band lamp (OSRAM) served as a standard for calibration. Down to 2300 Å the calibrated line intensities of a Rössler Standard Lamp (Philips) [3, 4] were employed. Lack of calibrated lines made a different method necessary in the region of 2300 Å to 2100 Å. Here the transmittance of the windows and the sensitivity of the photomultiplier is taken from manufacturer's data. The transmission of the monochromator with the collimating lens system was found by moving both pieces in and out of a path of light which passed through a second static mnochromator tuned to the same wavelength.

The entrance slit is adjusted so that the ionizing radiation is parallel to it and passes in front of it. With increasing gas pressure the absorption of light is concentrated close to the point where the light enters the chamber (exponential law). Correspondingly the origin of fluorescence also is increasingly concentrated around there. Since this concentration results in uneven illumination of the entrance slit, it is necessary to measure the degree to which detector system sensitivity is dependend on the source of the fluorescence. This has been accomplished with a movable point light source.

Franck-Condon-Factors

If some approximations are accepted, FC-factors can be employed for the description of transition probabilities of diatomic molecules [5]. So the electronic part of the transition moment R_e is taken to be independent of the internuclear distance r. Also the influence of rotation upon FC-factors is normally assumed to be negligible. It is in fact very small for CO, N_2, and O_2 [6] due to the small rotational constants.

The sum rule for the FC-factors $q_{v'v''}$ requests

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = \sum_{v'} [\int \Psi_{v'} \Psi_{v''} \, dr]^2 = \sum_{v''} [\int \Psi_{v'} \Psi_{v''} \, dr]^2 = 1 . \quad (1)$$

All FC-factors belonging to a common upper or lower vibrational level add up to unity. The fluorescence intensity $\Phi_{v'v''}$ (photons/second) of ionic states is

$$\Phi_{v'v''} = A(v') \cdot \lambda_{v'v''}^{-3} \cdot D(\lambda_{v'v''}) \cdot q_{v'v''} . \quad (2)$$

$A(v')$ contains the constants of the experimental setup, the electronic part of the transition moment, and the FC-factors $q_{v'}$ for the ionizing transition from the vibrational ground state of the neutral molecule into the state v' of the molecular ion. The population of the primary ionic species which depends upon $q_{v'}$ is calculated by summation over all fluorescence originating from the upper state v'. $q_{v'}$ is thus

$$q_{v'} = \sum_{v''} \frac{\Phi_{v'v''}}{D(\lambda_{v'v''}) \, B} \quad (3)$$

with

$$B = \sum_{v'} \sum_{v''} \frac{\Phi_{v'v''}}{D(\lambda_{v'v''})} . \quad (4)$$

These values $q_{v'}$ will be compared with results of photoelectron spectroscopy experiments which also employ a He I resonance line light source.

Transition probabilities have been measured for N_2^+ and CO^+. The He I resonance line ionizes ground state $N_2\,X\,^1\Sigma_g^+$ into the states $X\,^2\Sigma_g^+$, $A\,^2\Pi_u$, and $B\,^2\Sigma_u^+$. The necessary excitation energy is 15.576 eV, 16.694 eV, and 19.745 eV, respectively. The secondary transitions [7] $A \rightarrow X$ (Meinel bands) and $B \rightarrow X$ (1. negative system) occur with emission of radiation. Meinel bands appear only weakly between 6100 Å and 9510 Å. During the long natural lifetime of 12 μs [8] most of the A-state ions are collisionally deactivated without emission of radiation even at a low gas pressure. Also the detector sensitivity decreases considerably above 6000 Å. The Meinel bands were not measured.

The potential energy curves of the states $N_2\,X$, $N_2^+\,X$, and $N_2^+\,B$ show minima at nearly the same internuclear distances, namely at 1.0976 Å, 1.1116 Å, and 1.078 Å, respectively [7]. (0,0)-transitions are therefore expected to dominate photoionization as well as fluorescence. Tables 2 and 3 contain our measured FC-factors for the transitions $N_2\,X + h\nu \rightarrow N_2^+\,B + e^-$ and $N_2^+\,B \rightarrow N_2^+\,X + h\nu'$ along with theoretical values [12] and experimental results of other authors who employed different techniques. We could not separate the (1,1)-emission line from the stray light of an emision line of the He light source spectrum. In this case the sum rule is satisfied assuming the corresponding theoretical FC-factor [12] to be correct. This procedure can only have a limited effect upon other values.

[3] J. P. MEHLTRETTER, Dissertation, Univ. Heidelberg 1962.
[4] F. RÖSSLER, Ann. Physik (VII) **1**, 122 [1958].
[5] G. HERZBERG, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, v. Nostrand. New York 1950.
[6] J. B. SHUMAKER, J. Quant. Spectr. Rad. Transf. **9**, 153 [1969].
[7] A. LOFTHUS, Spectroscopic Rept. No. 2, Dept. of Physics, Univ. of Oslo, Blindern, Norway 1960.
[8] M. HOLLSTEIN, D. C. LORENTS, J. R. PETERSON, and J. R. SHERIDAN, Can. J. Chem. **47**, 1858 [1969].

Table 2. Franck-Condon-factors for the transition $N_2\,X\,^1\Sigma_g^+ + h\nu \rightarrow N_2^+\,B\,^2\Sigma_u^+ + e^-$.

(v', v'')	Turner and May[9] photoelectrons	Thomas et al.[10] fluorescence excitation with p^+	Aarts et al.[11] fluorescence excitation with e^-	This work fluorescence excitation with $h\nu$	Nicholls[12] theoretical
(0,0)	0.90	0.907	0.886	0.878 ± 0.015	0.891
(0,1)	0.10	0.091	0.112	0.118 ± 0.015	0.105

Table 3. Franck-Condon-factors for the transition $N_2^+\,B\,^2\Sigma_u^+ \rightarrow N_2^+\,X\,^2\Sigma_g^+ + h\nu'$.

(v', v'')	Thomas et al.[10] p^+ impact	Aarts et al.[11] e^- impact	Judge and Weissler[13] photon impact	This work photon impact	Nicholls[12] theoretical
(0,0)	0.641	0.644	0.57 ± 0.04	0.628 ± 0.012	0.651
(0,1)	0.259	0.269	0.30 ± 0.05	0.274 ± 0.014	0.259
(0,2)	0.083	0.067	0.10 ± 0.06	0.078 ± 0.010	0.070
(0,3)	0.016	0.016	0.03 ± 0.02	0.016 ± 0.005	0.016
(1,0)	0.233	0.281	0.19 ± 0.06	0.224 ± 0.012	0.301
(1,1)	0.210	0.246	0.29 ± 0.04	—	0.223
(1,2)	0.296	0.292	0.33 ± 0.06	0.326 ± 0.030	0.286
(1,3)	0.190	0.123	0.20 ± 0.06	0.169 ± 0.035	0.132
(1,4)	0.056	—	—	—	0.043

CO is isoelectronic to N_2. This results in similar excited states. They differ, however, with respect to symmetry operations. The He I resonance radiation produces the ionic states $CO^+\,X\,^2\Sigma^+$ (14.01 eV), $A\,^2\Pi_i$ (16.53 eV), and $B\,^2\Sigma^+$ (19.67 eV) [14]. Excitation is followed by emission of the bands $A \rightarrow X$, $B \rightarrow X$, and $B \rightarrow A$. The first negative system $B \rightarrow X$ consists of very strong lines between 2000 Å and 3100 Å. It has already been pointed out that it is difficult to calibrate a detector system in this region of wavelength. Aarts and De Heer [15] proposed that the CO^+ 1. negative system should be used for calibration. Only the exact FC-factors need to be known. Calibration could most easily be realized with electron impact ionization. It is thus very important to check experimental electron impact data with a method which does not allow the occurence of cascades that migth populate the CO^+ B state. Photoionization is well suited. If both methods lead to identical FC-factors the easier electron impact ionization may well be applied for calibration.

Tables 4 and 5 list FC-factors for the transition $CO\,X + h\nu \rightarrow CO^+\,B + e^-$ and $CO^+\,B \rightarrow CO^+\,X + h\nu'$. They agree in nearly all cases with theoretical data and FC-factors from electron impact ionization.

The Baldet-Johnson system $B \rightarrow A$ occurs so weakly between 3000 Å and 4300 Å that no FC-factors were measured. This transition, however, changes the primary $CO^+\,A$ population. For two reasons this effect is only a negligible source of error. First, 99% of the B-state ions emit according to the $B \rightarrow X$ transition rather than according to the $B \rightarrow A$ transition. Second, the primary population of the A-state due to photoionization is very

[9] D. W. Turner and D. P. May, J. Chem. Phys. **45**, 471 [1966].
[10] E. W. Thomas, G. D. Bent, and J. L. Edwards, Phys. Rev. **165**, 32 [1968].
[11] J. F. M. Aarts, F. J. DeHeer, and D. A. Vroom, Physica **40**, 197 [1968].
[12] R. W. Nicholls, J. Res. A **65**, 451 [1961].
[13] D. L. Judge and G. L. Weissler, J. Chem. Phys. **48**, 4590 [1968].
[14] P. H. Krupenie, The Band Spectrum of Carbon Monoxide, NBS, NSRDS-NBS 5, Washington 1966; J. Chem. Phys. **43**, 1529 [1965].
[15] J. F. M. Aarts and F. J. DeHeer, J. Opt. Soc. Amer. **58**, 1666 [1968].
[16] J. F. M. Aarts and F. J. DeHeer, Physica **49**, 425 [1970].
[17] M. C. Poulizac, J. Desesquelles, and M. Dufay, Ann. d'Astrophysique **30**, 301 [1967].
[18] R. W. Nicholls, J. Phys. B **1**, 1192 [1968].
[19] F. Stuhl, D. Kley, and H. Niki, to be published.
[20] D. C. Jain and R. C. Sahni, J. Quant. Spectr. Rad. Transf. **6**, 705 [1966].

Table 4. Franck-Condon-factors for the transition $CO\ X\ ^1\Sigma^+ + h\nu \rightarrow CO^+\ B\ ^2\Sigma^+ + e^-$.

(v'', v')	Turner and May[9] photoelectrons	Aarts and De Heer[16] fluorescence excitation with e^-	Poulizac et al.[17] fluorescence excitation with p^+	This work fluorescence excitation with $h\nu$	Nicholls[18] theoretical
(0,0)	0.63	0.684	0.732	0.68 ± 0.01	0.687
(0,1)	0.28	0.253	0.205	0.25 ± 0.01	0.249
(0,2)	0.08	—	—	0.06 ± 0.01	0.053

Table 5. Franck-Condon-factors for the transition $CO^+\ B\ ^2\Sigma^+ \rightarrow CO^+\ X\ ^2\Sigma^+ + h\nu'$.

(v', v'')	Stuhl et al.[19] collisions 2nd	Aarts and De Heer[16] e^- impact	Poulizac et al.[17] p^+ impact	This work photon impact	Jain and Sahni[20] theoretical
(0,0)	0.51	0.55	0.60	0.51 ± 0.02	0.538
(0,1)	0.38	0.34	0.25	0.36 ± 0.02	0.335
(0,2)	0.097	0.096	0.052	0.10 ± 0.01	0.102
(0,3)	0.016	0.017	0.016	0.020 ± 0.005	0.020
(1,0)	0.28	0.34	0.29	0.28 ± 0.02	0.315
(1,1)	0.055	0.060	0.075	0.066 ± 0.010	0.065
(1,2)	0.33	0.32	0.39	0.35 ± 0.02	0.319
(1,3)	0.24	0.20	0.15	0.21 ± 0.02	0.212
(1,4)	0.059	0.063	0.075	0.075 ± 0.010	0.070
(2,1)	0.28	—	0.32	0.25 ± 0.02	0.273
(2,3)	0.20	—	0.15	0.16 ± 0.01	0.160
(2,4)	0.29	—	0.22	—	0.255
(2,5)	0.13	—	0.14	0.14 ± 0.010	0.138

strong and is thus not affected by a small component originating from the cascade.

The Comet-tail system $CO^+\ A \rightarrow X$ extends from 2300 Å to the infrared. 75% of the total emission intensity lies outside the range of the detector system sensitivity. Therefore the values in Table 6 are no FC-factors, but emission probabilities which have been normalized to unity for the (3,0)-transition. The values are proportional to the FC-factors for absorption $q_{v'}$ and emission $q_{v'v''}$ as well as to the third power of the emitted radiation energy. The CO^+ A states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ differ considerably in

Table 6. Emission probabilities for the transition $CO^+\ A\ ^2\Pi_i \rightarrow CO^+\ X\ ^2\Sigma^+ + h\nu'$.

(v', v'')	Aarts and De Heer[16] e^- impact	Poulizac et al.[17] p^+ impact	This work photon impact	Nicholls[18], Jain, Sahni[20] theoretical
(0,0)	—	0.26	0.04 ± 0.01	0.052
(1,0)	—	0.84	0.42 ± 0.05	0.393
(1,1)	0.54	0.92	0.39 ± 0.05	0.488
(2,0)	1.08	1.35	0.97 ± 0.10	0.864
(2,1)	0.42	0.67	0.45 ± 0.05	0.381
(3,0)	1.00	1.00	1.00 ± 0.10	1.000
(3,2)	—	0.274	0.19 ± 0.05	0.228
(4,0)	0.69	0.68	0.75 ± 0.10	0.767
(5,0)	0.38	0.24	0.46 ± 0.05	0.441
(5,2)	—	—	0.11 ± 0.03	0.109
(5,3)	—	—	0.06 ± 0.02	0.055
(6,0)	0.16	—	0.17 ± 0.04	0.204
(7,0)	0.056	—	0.07 ± 0.02	0.078
(7,1)	0.082	—	0.14 ± 0.04	0.114
(8,0)	—	—	0.02 ± 0.01	0.028
(8,1)	—	—	0.05 ± 0.02	0.063

energy. Mostly the transitions with the longer wavelength, namely $^2\Pi_{3/2} \rightarrow {}^2\Sigma_{1/2}$ are more intensive than those corresponding to $^2\Pi_{1/2} \rightarrow {}^2\Sigma_{1/2}$. The emission intensities shown in Table 6 are based upon the total intensities integrated over both transitions.

Deactivation Cross Sections

Determination of FC-factors is falsified if the primary population of excited states is changed by secondary effects. As pointed out, cascades are one such secondary effect, collisions of the excited particles are another. Particularly in the case of ionic species collision cross sections are expected to be large, because electric attractive forces caused by polarization play a role. The deactivation cross sections can, however, be calculated from collisional quenching, if the natural lifetime τ of the species is known. Collisional processes can thus be examined for excited particles. Luminescence measurements are therefore valuable supplements to beam experiments which, because of the inherent time of flight, are restricted to non excited or at least long living particles.

Collisional deactivation cross sections were measured for the following ionic species:

N_2^+ B $v' = 0$ and 1	in collision with N_2 and O_2,
CO^+ B $v' = 0$, 1, and 2	in collision with CO,
CO^+ A $v' = 0$ to 8	in collision with CO,
O_2^+ b $\Delta v = 1$ and 2	in collision with O_2.

Production of O_2^+ b $^4\Sigma_g$ needs a photon energy of at least 18.2 eV [21].

The first negative system leads to the O_2^+ a $^4\Sigma_u$-state. The fluorescence has been measured. The rotational distribution is very wide whereas the band heads of different transitions are very close together. Therefore part of the luminescence can not be resolved. This is the case for all transitions of equal difference Δv in vibrational quantum numbers. So, e. g. the transitions with $\Delta v = 1$, i. e. (1,0), (2,1), (3,2) etc. overlap. The same is true for $\Delta v = 2$, 3, etc.

Figures 3 and 4 show the measured deactivation cross sections σ. It has been assumed that the collision partner is neutral and in its ground state.

[21] F. R. GILMORE, J. Quant. Spectr. Rad. Transf. 5, 369 [1965].

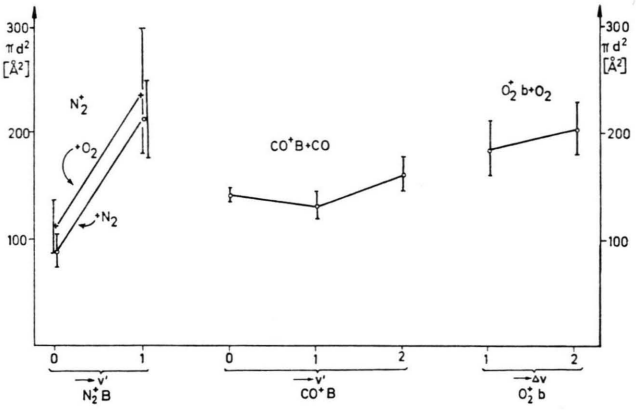

Fig. 3. Collisional deactivation cross section πd^2 as a function of vibrational quantum number v' for N_2^+ B colliding with N_2 and O_2, and for CO^+ B and O_2^+ b colliding with their parent molecules, respectively (see also the data of [23, 24, 33]).

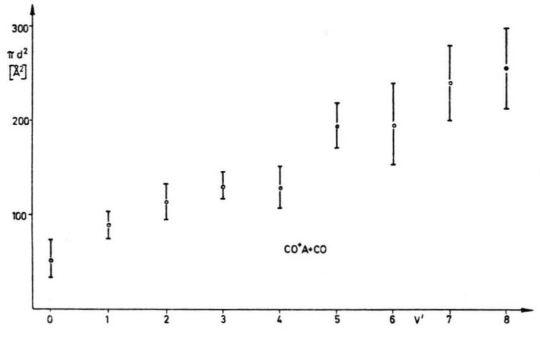

Fig. 4. Collisional deactivation cross section πd^2 as a function of vibrational quantum number v' for CO^+ A colliding with CO (see also the data of [23, 24, 33]).

A bimolecular collision can affect an excited molecular ion $(AB^+)^*$ which has been produced according to (5 a) and would if no collision partner were present radiate according to (5 b).

$$
\begin{aligned}
&AB + h\nu \longrightarrow (AB^+)^* + e^-, && \text{(a)}\\
&(AB^+)^* \xrightarrow{k_b} AB^+ + h\nu', && \text{(b)}\\
&(AB^+)^* + M \xrightarrow{k_c} \text{products without luminescence of } h\nu', && \text{(c)}\\
&(AB^+)^* + M \xrightarrow{k_d} AB^+ + M + h\nu'. && \text{(d)}
\end{aligned}
\qquad (5)
$$

The collision can lead to induced fluorescence (5 d). Also the excitation energy can be used for a reaction or can be transduced onto the collisional partner (5 c). Equation (5) does not include processes which result in emission other than at frequency ν'. In case there are higher excited ions that may populate the state $(AB^+)^*$ (cascades) Eq. (5 a)

has to be completed by (6).

$$(AB^+)^{**} \rightarrow (AB^+)^* + h\nu'', \quad \text{(a)}$$
$$(AB^+)^{**} + M \rightarrow (AB^+)^* + M + h\nu''. \quad \text{(b)} \qquad (6)$$

Equation (7) shows the interdependence of the measured fluorescence intensities Φ_E (photons/s) and the rate constant k_c if we assume that (5 b) and (5 c) completely describe the deactivation. Φ_A and Φ_E are the number of absorbed or emitted photons per unit of time.

$$\Phi_A/\Phi_E = 1 + k_c C p_M/k_b . \qquad (7)$$

If the ion is deactivated by the parent molecule AB the particle density $[M] = C p_M$ of the collision partner may approximately be replaced by the particle density $C p$ of AB. With

$$k_b = 1/\tau .$$

(7) leads to

$$\Phi_A/\Phi_E = 1 + C p k_c \tau \qquad (8)$$

and

$$C p k_c = (\Phi_A/\Phi_E - 1) \cdot 1/\tau . \qquad (9)$$

$C p k_c$ is the mean lifetime of the particle $(AB^+)^*$ with respect to collisional deactivation. The mean free path $\bar{\lambda}$ with respect to collisional deactivation depends upon the mean speed v_0 of the particles.

$$\lambda = \tau v_0 \sqrt{T/T_0}/(\Phi_A/\Phi_E - 1). \qquad (10)$$

The kinetic theory expression for $\bar{\lambda}$ is

$$\lambda = 0.957/\sqrt{2}\, n \pi d^2. \qquad (11)$$

The deviation of the numerator from unity takes into account Tait's correction [22] which has to be applied in this case. The cross section πd^2 for collisional deactivation is therefore

$$\pi d^2 = 0.957 (\Phi_A/\Phi_E - 1)/\tau \sqrt{2}\, n v_0 \sqrt{T/T_0} . \qquad (12)$$

Equation (12) is valid for a thermal distribution at temperature T.

All values of Figs. (3) and (4) are calculated from Stern-Volmer-diagrams based upon Equation (8). Φ_A/Φ_E is plotted as a function of pressure p. The bimolecularity of the deactivating collisions follows from the exact linearity which extends over two to three orders of magnitude. As an example Fig. 5 a and b show the Stern-Volmer-diagram for the transition $CO^+ A(v' = 2) \rightarrow CO^+ X(v'' = 0) + h\nu'$. The slope is a measure for k_c and thus the collisional deactivation cross section πd^2. The lifetimes τ

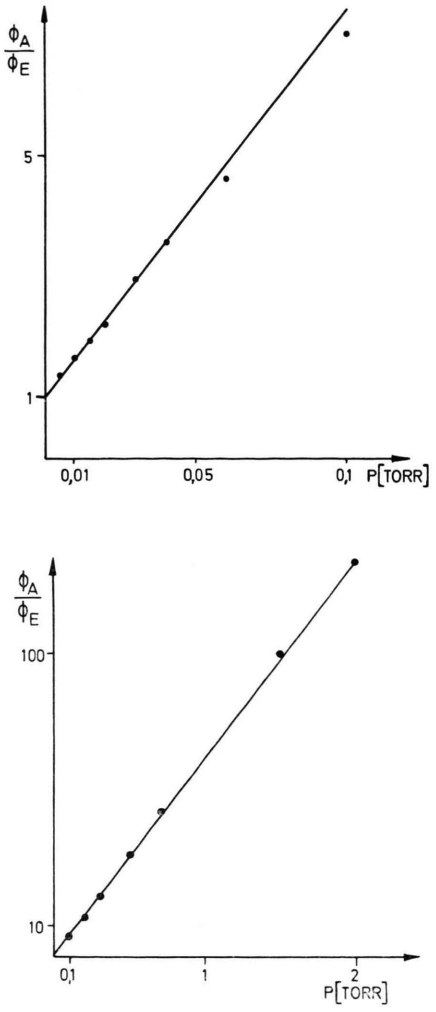

Fig. 5. Stern-Volmer-diagram for the transition $CO^+ A\ (v'=2) \rightarrow CO^+ X\ (v'=0) + h\nu$, a) low pressure, b) high pressure.

have been accepted from various authors. ($N_2^+ B$ [23], $CO^+ A$ [24], $CO^+ B$ [23], $O_2^+ b$ [24].)

Lifetimes of $CO^+ A\ v' = 0$ and $v' = 8$ have not yet been measured. The values 2760 ± 200 ns and 1460 ± 400 ns were taken from a linear extrapolation of the values for $v' = 1$ to 7 [24]. This procedure appears to be valid because the measured values lie on a straight line. When possible the cross section of one particular state was measured for transitions into various lower states, e. g. (1, 0) and (1, 1). As expected the results were equal within the limits of

[22] P. G. TAIT, Trans. Roy. Soc. Edinb. **33**, 65 [1886].
[23] J. E. HESSER, J. Chem. Phys. **48**, 2518 [1968].
[24] E. H. FINK and K. H. WELGE, Z. Naturforsch. **23 a**, 358 [1968].

error. The results also did not differ when the $J=3/2$ or $J=1/2$ states were investigated. The extent of error indicated in the figure originates mostly from the uncertainty in lifetime.

Only a limited part of the chamber lies within the range of the spectrometer. According to the Lambert-Beer-law the fraction of the incident radiation Φ_A which is absorbed here, depends upon pressure. Therefore the absorption coefficient μ of the gases at $\lambda=584$ Å is of primary importance. Considerable difference between the results reported by different authors, made a new determination necessary. The coefficients containend in Table 7 result in linear Stern-Volmer-plots for all transitions of the gases in question. The fact that the Stern-Volmer-plots for all examined transitions can be linearized by a suitable choice of the absorption coefficient, also makes sure that the deactivation of the excited ions is completely described by Eqs. (5 b) and (5 c). Processes like (5 d) lead to deviations from linearity which vary for different vibrational and electronic states. Three-body-collisions even bend Stern-Volmer-plots in such a way that they can by no means be linearized by a different choice for μ. This process should be excluded, as well as process (6).

Table 7. Absorption coefficients at $\lambda=584$ Å.

CO	N_2	O_2
$610 \pm 40\ cm^{-1}$	$700 \pm 40\ cm^{-1}$	$670 \pm 40\ cm^{-1}$

Discussion

The size of the deactivation cross sections shows clearly that it is necessary to extrapolate measured fluorescence intensity ratios to $p=0$, in order to receive correct FC-factors. Discrepancies between the results of this work and other authors are therefore favoured to arise especially for transitions which originate in long living states, as e. g. for $CO^+ A\,^2\Pi \rightarrow CO^+ X\,^2\Sigma^+ + h\nu'$. $CO^+ A$ has a mean lifetime of 2 μs [24]. At a pressure of 0.1 Torr already about 90% of the fluorescence is quenched. For FC-factor measurements with an incident radiation energy far above the required excitation energy another error is caused by cascades from higher states which change the relative luminescence intensities. Even for 100 eV electrons cascades can not be excluded.

For most of the investigated transitions the FC-factors of this work agree with theoretical results. This is especially true for the photoabsorption process. FC-factors for absorption and emission are based upon the same luminescence spectrum and thus incorporate the same experimental errors. FC-factors for absorption stem from a summation of all fluorescence intensities originating from a common upper vibrational state. Systematic errors in the determination of the detector wavelength dependence $D(\lambda)$ might cancel for these sums which extend over a large range of the spectrum. Such error will falsify, however, FC-factor-determination for the emission process. Accordingly experimental FC-factors for absroption are found to agree closer with theoretical values than emission FC-factors, though even most of these also prove the validity of the theoretical values within the experimental limits of error.

The deactivation of N_2^+ B-state ions in collision with N_2 was already discussed in a previous publication [25]. We argued that the deactivation mechanism which results in quite different cross sections for $v'=0$ and $v'=1$, is governed by a radiationless transition of the ion into the closest lying vibrational level of the lower A-state. The collision was regarded as a perturbation by which the transition is made possible. Bimolecular reactive collisions are excluded at the excitation energy used in the experiment. The low electron density does not allow electron-ion recombination to be of importance. The new results obtained for N_2^+ B deactivated in collisions with O_2 (Fig. 3) strongly supports the argument. Obviously both gases, N_2 and O_2, are equally effective in the collisional deactivation of N_2^+ B. Ion molecule reactions are known to occur for N_2^+ with O_2 [26] but have only been observed for N_2^+ A. Figure 3 shows, however, that their participation in the deactivation is only little. The equal effectiveness of N_2 and O_2 in the deactivation of N_2^+ B is very similar to the results of MOORE and DOERING [26a] in charge exchange collisions, who found their pro-

[25] F. J. COMES and F. SPEIER, Chem. Phys. Lett. **4**, 13 [1969].
[26] E. W. MCDANIEL, V. ČERMÁK, A. DALGARNO, E. E. FERGUSON, and L. FRIEDMAN, Ion-Molecule Reactions, J. Wiley & Sons, Interscience, New York 1970.
[26a] J. H. MOORE, JR. and J. P. DOERING, Phys. Rev. **177**, 218 [1969].

cesses to be independent of the chemical nature of the projectiles.

For the investigated molecular ions the results favour a deactivation mechanism which explains deactivation by collision induced radiationless transitions into other electronic states. The ion in the resulting state does either not radiate (e. g. ground state) or radiation occurs in a spectral region which is not observable in the experiment. Deactivation has to be regarded as a collision induced transition of internal energy within the excited molecular ion. At the excitational and translational energy available in this experiment no reactive collisions are known for the systems (CO^+; CO) and (O_2^+; O_2). The probability for vibrational relaxation has been found to be only small for systems similar to the investigated ones [27]. They are also strongly excluded by the linearity of the Stern-Volmer-plots.

Charge exchange for collisions of N_2^+ ground state ions with N_2 has been measured to occur with nearly equal cross sections [28] as compared with the results of this work. Figure 3, however, does not make charge exchange seem to be very probable. This statement is further supported by the measured dependence of the cross section as a function of the kinetic energy of the ions, which is to be described in a future publication [29]. If the theory [30] which has been developed for ground state atomic ions can also be applied to molecular systems [31], the deactivation cross sections should first increase with kinetic energy of the ions in case of non-resonance. Instead, an exponential decrease has always been measured. Also, a stronger dependence of the cross section upon vibrational energy should be expected.

In detail the following transitions are expected to contribute essentialy to the deactivation of the investigated excited molecular ions:

$$
\begin{aligned}
&\text{(a)}\quad N_2^+\,B\,{}^2\Sigma_u^+ + N_2 \rightarrow N_2^+\,A\,{}^2\Pi_u + N_2\,,\\
&\text{(b)}\quad N_2^+\,B\,{}^2\Sigma_u^+ + O_2 \rightarrow N_2^+\,A\,{}^2\Pi_u + O_2\,,\\
&\text{(c)}\quad CO^+\,B\,{}^2\Sigma^+ + CO \rightarrow CO^+\,A\,{}^2\Pi_i + CO\,,\\
&\text{(d)}\quad CO^+\,A\,{}^2\Pi_i + CO \rightarrow CO^+\,X\,{}^2\Sigma^+ + CO\,, \qquad (13)\\
&\text{(e)}\quad O_2^+\,b\,{}^4\Sigma_g^- + O_2 \rightarrow O_2^+\,A\,{}^2\Pi_u + O_2\,,\\
&\text{(f)}\qquad\qquad\quad \rightarrow O_2^+\,a\,{}^4\Pi_u + O_2\,.
\end{aligned}
$$

Differences in electronic energy will lead to vibrational excitation of the final state. Rotation which is definitely of importance for these processes is not discussed here because the measurement of rotational excitation is not possible with the available intensity.

The cross sections for the deactivation of the excited molecular ions will be predominantly given by the interaction of the ions with the induced dipole of the collision partners. Obviously, cross sections become larger when the potential energy curves for the original and the final states are close to each other. Exact energy resonance does not seem to play an important role. No correlation could be found between the size of cross sections and the energetical difference between the primary ionic states and various possible final states. Quasi-resonance which includes rotational excitation can, however, not strictly be excluded.

The present argumentation that the collision can be described by inspecting the potential energy curves of the isolated particles, is a crude approximation. On the other hand, an exact description in terms of a many body problem is extremely difficult.

The repulsive limbs of the potential energy curves for the B- and A-state of N_2^+ are close to each other and cross for $v' = 3$ under a small angle [21]. The collisional cross section is therefore expected to increase strongly for $v' > 0$. The potential energy curves for the A- and X-state of CO^+, however, cross at internuclear distances $R > R_0$ with a maximal overlap at $v' = 7$ [14]. In accordance with this Fig. 3 and 4 show a rapid rise in the deactivation cross section for N_2^+ B but only a slower increase for CO^+ A.

The potential energy curves for the CO^+ B- and O_2^+ b-states are relatively far away from possible final states [14, 21]. Only little, if any, dependence of the cross section upon vibrational energy is expected, and also found as Fig. 3 shows.

Our hypothesis is supported by measurements of the collisional deactivation of excited molecules in neutral states, reported by other authors. HARTFUSS and SCHMILLEN [32] found maximal quenching of the $N_2\,B\,{}^3\Pi_g$-state for $v' = 4$. This coincides exactly with maximum overlap of the states $N_2\,B\,{}^3\Pi_g$ and

[27] H. SHIN, in: Ion Molecule Reactions in the Gas Phase, p. 44, ed. P. J. AUSLOOS, American Chemical Soc., Washington D.C. 1966.

[28] J. J. LEVENTHAL, T. F. MORAN, and L. FRIEDMAN, J. Chem. Phys. **46**, 4666 [1966].

[29] F. J. COMES and F. SPEIER, to be published.

[30] D. RAPP and W. E. FRANCIS, J. Chem. Phys. **37**, 2631 [1962].

[31] M. J. HAUGH and K. D. BAYES, Phys. Rev. A **2**, 1778 [1970].

[32] H. J. HARTFUSS and A. SCHMILLEN, Z. Naturforsch. **23 a**, 722 [1968].

$A\,^3\Sigma_u^+$ [21]. Their measurements for the $a'\,^3\Sigma^+$-state can equally be interpreted. BROCKLEHURST and DOWNING ($N_2\,C\,^3\Pi_u$) [33] report equivalent results.

The selection rules should also be discussed in this connection. If the process can be handled as a radiationless transition, the selection rules $u \longleftrightarrow u$, $g \longleftrightarrow g$ and $\Delta S = 0$ hold [5]. They are, however, less strict for heavy particles. Furthermore, polarisation results in electric fields of such a high strength that the symmetry of the states involved is destroyed. It is therefore well understandable that collisional deactivation processes occur even when violating the above-mentioned selection rules *.

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[33] B. BROCKLEHURST and F. A. DOWNING, J. Chem. Phys. **46**, 2976 [1967].

* *Note added in proof:* To Fig. 3 and 4 see also: G. DAVIDSON and R. O'NEIL, Report AFCRL-67-0277 [1968]; M. JEUNEHOMME, J. Chem. Phys. **44**, 4253 [1966]; K. B. MITCHELL, J. Chem. Phys. **53**, 1795 [1970]; M. N. HIRSH, E. POSS, and P. N. EISNER, Phys. Rev. **1A**, 1615 [1970].

Die Beeinflussung der optischen Absorption von Molekülen durch ein elektrisches Feld

X. Erweiterung der Theorie unter Berücksichtigung der Fluktuationen der effektiven elektrischen Felder *

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The optical properties of molecules may be affected by an electric field. With suitable molecules, these effects allow to determine the electric dipole moments and certain components of the polarizability tensors in the ground state and in excited electronic states, the directions of transition moments and certain components of the transition polarizability tensors. The magnitude of the electrooptical effects depends on the effective electric field acting on the molecule. In preceding papers the representation of the effective field was based on the Onsager model. More recent experimental investigations have shown that this approximation is not sufficient when using polar solvents. Here, local fluctuations of the electric field have to be taken into account. Basing on previous theories, an extension including these effects is developed which agrees with the experimental results, as will be shown in the following paper [7]. Also, an approximate expression is derived for the mean square of the effective electric field.

Die optischen Eigenschaften von Molekülen können durch ein elektrisches Feld beeinflußt werden; die in einem äußeren elektrischen Feld auftretenden Effekte werden unter dem Begriff Elektrochromie zusammengefaßt [1]. Die Änderungen der optischen Absorption können durch Überlagerung von drei Effekten, nämlich dem Orientierungseffekt, dem Bandenverschiebungseffekt und der direkten Feldabhängigkeit des Übergangsmoments, beschrieben werden. Die Auswertung von elektrooptischen Absorptionsmessungen [2,3] kann bei geeigneten Molekülen eine Bestimmung der Übergangsmomentrichtung der untersuchten Absorptionsbande, des elektrischen Dipolmoments und bestimmter Komponenten der Polarisierbarkeit des Moleküls im Grund- und Elektronenanregungszustand sowie von bestimmten Komponenten der Übergangspolarisierbarkeit erlauben.

Für die Größe der elektrooptischen Effekte ist das effektive Feld am Ort des gelösten Moleküls maßgebend. In den bisherigen Untersuchungen wurde das effektive Feld auf Grundlage des Onsagerschen Modells als Summe des Hohlraumfelds und des Reaktionsfelds des Moleküls dargestellt [4–6]. Für die

* Mitteilung IX, Angew. Chem. **81**, 195 [1969].

[1] W. LIPTAY, Angew. Chem. **81**, 195 [1969]; Intern. Edit. **8**, 177 [1969].

[2] H. LABHART, Chimia **15**, 20 [1961].

[3] W. LIPTAY, W. EBERLEIN, H. WEIDENBERG u. O. ELFLEIN, Ber. Bunsenges. physik. Chem. **71**, 548 [1967].

[4] W. LIPTAY, Z. Naturforsch. **20a**, 272 [1965].

[5] W. LIPTAY, Modern Quantum Chemistry, Part 3, 45, Academic Press, New York 1965.

[6] W. LIPTAY, B. DUMBACHER u. H. WEISENBERGER, Z. Naturforsch. **23a**, 1601 [1968].

[7] W. LIPTAY, G. WALZ, W. BAUMANN, H.-J. SCHLOSSER, H. DECKERS u. N. DETZER, Z. Naturforsch. **26a**, 2020 [1971]; nachstehende Arbeit.