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Rotational Excitation of Reaction Products: $C^+ + O_2 \rightarrow CO^+ (A\ ^2\Pi) + O$

Ch. Ottinger and J. Simonis
Max-Planck-Institut für Strömungsforschung, Göttingen, Germany

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Chemiluminescent reactions between C^+ and O_2 were studied in a beam experiment. At $E_{c.m.} = 3.6$ eV, $CO^+(A\ ^2\Pi)$ is formed with abnormally high rotational excitation.

Chemiluminescence is a convenient way of studying excited products of bimolecular gas-phase reactions with high precision. Infrared chemiluminescence has even revealed the rotational excitation of reaction products.[1] Here we are reporting on a uv-chemiluminescent ion-molecule reaction, a type of process which has only recently come under study.[2,3] In this work rotational excitation of the products of an ion-molecule reaction was directly observed for the first time.

The formation of CO^+ ions in $C^+ + O_2$ collisions is known from mass-spectrometric work.[4-6] Measurements of the translational endoergicity showed that energies up to several eV could be stored in the product ion.[6] This suggested a search for emission from the known electronically excited states $CO^+(A\,^2\Pi)$ or $CO^+(B\,^2\Sigma^+)$.

Our apparatus consists of a plasma ion source, magnetic mass separator, collision chamber, optical spectrometer, photomultiplier, and photon-counting system. The C^+ ions were produced from CO; their energy in the collision chamber was varied between 1 and 1000 eV with a spread of about 0.9 eV full width at half-maximum and an absolute uncertainty, due to plasma and surface charges, of about 1 eV. The target-gas pressure was 10^{-2} Torr; the observed emission intensity varied linearly with the pressure between 2×10^{-4} and 1.6×10^{-2} Torr. The beam current into the collision chamber was 2×10^{-9} A at $E_{lab} = 5$ eV. The emission spectra were scanned repetitively from 1800 to 5000 Å with an optical resolution of 20 Å and signal averaged for up to 20 h.

At high collision energy the emission consisted mainly of $O_2{}^+$ band systems. They disappeared below 25 eV_{lab}.[7] A typical low-energy result is shown in Fig. 1(a) for a collision energy of $E_{lab} = 5$ eV, corresponding to $E_{c.m.} = 3.6$ eV. This spectrum is due to the $CO^+(A\,^2\Pi \rightarrow X\,^2\Sigma^+)$ transition,[8,9] where the CO^+ ions are formed in the reaction

$$C^+ + O_2 \rightarrow CO^+(A\ ^2\Pi) + O. \tag{1}$$

There is no clear evidence of $CO^+(B\,^2\Sigma^+)$ emission.

For comparison, Fig. 1(b) shows a $CO^+(A \rightarrow X)$ spectrum which was excited by charge transfer

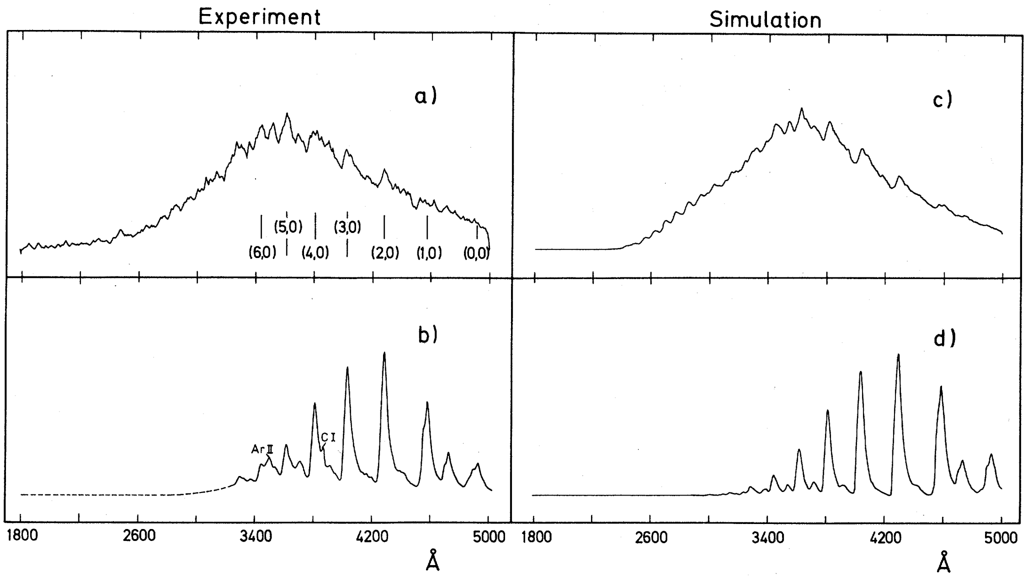

FIG. 1. $CO^+(A\,^2\Pi \rightarrow X\,^2\Sigma^+)$ ("comet tail") spectra from (a), (c), the luminescent ion-molecule reaction $C^+ + O_2 \rightarrow CO^{+*} + O$ at $E_{lab} = 5$ eV and (b), (d), the charge transfer reaction $Ar^+ + CO \rightarrow CO^{+*} + Ar$ at $E_{lab} = 1000$ eV. The experimental spectra are shown on the left-hand side. The resolution was 20 Å in both (a) and (b). Some tabulated band heads of the $CO^+(A \rightarrow X)$ system are indicated. Ar II and C I mark two spectral lines which do not belong to the CO^+ emission. The dashed portion was not measured. Spectra simulated by computer are given on the right-hand side. The rotational distributions assumed in the simulations were thermal with $T = 45\,000$°K (c) and 1000°K (d). For details, also on the vibrational distributions, see text.

at $E_{lab} = 1000$ eV:

$$Ar^+ + CO \rightarrow Ar + CO^+(A\,^2\Pi). \qquad (2)$$

In this spectrum the bands of the well-known $(v',0)$ progression are clearly separated, while in Fig. 1(a) they are broadened to the point of being almost indistinguishable. This reflects an extreme rotational excitation of the reactively produced CO^+, as compared to the charge transfer shown in Fig. 1(b) (see below).

The electronic states of the reactant C^+ and product O in Eq. (1) need to be discussed. Earlier work indicates that C^+ beams generated from CO with electrons of 50–100 eV contain typically 15 to 30% of metastable $C^+(^4P)$, besides the $C^+(^2P^0)$ ground-state ions.[4,5] The appearance potentials of $C^+(^2P^0)$ and $C^+(^4P)$ from CO are 22.5 and 27.8 eV, respectively.[10,11]

As the ionizing voltage in the ion source was lowered to less than about 30 V, the CO^+ light yield, normalized to the total C^+ current, rose by about 20%.[7] This can be understood if $C^+(^4P)$ is present in about 20% concentration at high electron energies, but is ineffective for the $CO^+(A\,^2\Pi)$ production. We therefore conclude that only ground-state C^+ ions contribute to Reaction (1). The experiments were then run at 80 eV ionizing energy in order to maximize the ion current from the source.

The identity of the product O atoms as $O(^3P)$ was inferred from cross-section measurements. Reaction (1) is exothermic by $\Delta E = 0.7$ eV if O is formed in its ground state $O(^3P)$. If $O(^1D)$ or $O(^1S)$ were produced, the reaction would be endothermic by 1.27 or 3.50 eV, respectively. Experimentally the cross section for $CO^+(A\,^2\Pi)$ production increased monotonically with decreasing energy[7] and at the lowest energy, $E_{c.m.} \approx 1$ eV, still showed no indication of a threshold. Therefore we conclude that ground-state O atoms are formed in Reaction (1), which then reads

$$C^+(^2P^0) + O_2(X\,^3\Sigma_g^-) \rightarrow CO^+(A\,^2\Pi) + O(^3P). \qquad (3)$$

In order to obtain a quantitative measure of the rotational excitation of $CO^+(A\,^2\Pi)$, the rearrangement and charge-transfer spectra, Figs. 1(a) and 1(b), were simulated by use of a computer (see also Ref. 1). The wavelengths of the individual rotational lines were calculated for the $CO^+(A \rightarrow X)$ system. Each line was assigned an intensity proportional to its line-strength factor[12] and to the Franck-Condon factors for the corresponding

$v' \to v''$ transition.[13] In addition, the line intensities were weighted with an assumed distribution $P(v', J')$. Then the intensities of all lines within the spectrometer bandwidth, $\Delta\lambda$, were summed and corrected for the detection sensitivity at λ. Comparing the resulting simulated spectra with the experimental ones, $P(v', J')$ was then adjusted to give a best overall fit.

$P(v', J')$ was taken to be of the form $P_1(v')(2J' + 1)\exp[-B_v'J'(J'+1)/kT]$, i.e., for computational convenience, a thermal rotational distribution was used. For simulation of the reactively produced spectrum, Fig. 1(a), the temperature T was scaled with v' according to $T \equiv T(v') = T_0[E_0 - G(v')]/E_0$, where E_0 is the total available energy, $E_0 = \Delta E + E_{\rm c.m.} = 4.3$ eV, and $G(v')$ is the vibrational energy. Also in this case $P(v', J')$ was truncated at the highest J' energetically accessible at each v'. For simulation of the charge-transfer spectrum, Fig. 1(b), T was simply set constant, $T = T_0$ for all v'. In both cases T_0 and the distribution $P_1(v')$ were left adjustable.

Varying these parameters, the spectra shown in Figs. 1(c) and 1(d) were finally arrived at as the best possible fits to the observed spectra. These simulations are based on the following distributions: $P_1(v')$ is, for the spectrum in Fig. 1(c), a function which decreases linearly from 1.0 (arbitrary units) at $v' = 0$ to 0.07 at $v' = 12$, and further to 0.05 at $v' = 24$ where it is truncated. For Fig. 1(d), $P_1(v')$ is of Boltzmann form with a vibrational temperature of 2100°K.

Of special interest are the corresponding rotational distributions. In Fig. 1(c), for the reactively formed $\mathrm{CO}^+(A\,{}^2\Pi)$, T_0 is as high as 45 000°K. In contrast to this, in Fig. 1(d) T_0 is only 1000°K. This shows that charge transfer produces very much less rotational excitation than does the reaction.[3, 14]

Note that the cutoff at the energy limit severely affects the shape of the rotational distribution underlying the spectrum of Fig. 1(c). With T_0 as high as 45 000°K the most probable J' is as much as $\frac{2}{3}$ of the J' limit imposed by energy requirements. Thus the truncated J' distribution differs greatly from a full thermal distribution. The shape of the simulated spectrum is then dominated by the cutoff value of J', while the exact choice of T_0 has little effect at these high "temperatures." For example, $T_0 = 28\,000$°K gave an almost equally good fit. $T_0 = 14\,000$°K, however, clearly did not give enough blurring of the individual bands.

With the energy cutoff dominating the rotational distribution, the overall band structure is expected to depend sensitively on the collision energy. This is indeed found: At $E_{\rm lab} = 8$ eV, where the total available energy, 6.3 eV, allows states up to $J' = 180\hbar$ to be populated, the band structure was observed to disappear completely as a result of rotational blurring.[7]

The angular momentum of $\mathrm{CO}^+(A\,{}^2\Pi)$, averaged over the best-fit distributions $P(v', J')$, is $78\hbar$ at $E_{\rm c.m.} = 3.6$ eV. The initial orbital angular momentum of C^+ and O_2 averages to about $L = 200\hbar$, if an equal reaction probability is assumed for all impact parameters out to the Langevin radius of 2.3 Å.[15] The initial rotational angular momentum of O_2 is only $J_{mp} = 9\hbar$. Thus about 40% of the initial orbital angular momentum reappears after the reaction in the form of product rotation.

For the energy balance at $E_{\rm c.m.} = 3.6$ eV our simulation yields average fractions of $f_v = 0.24$ and $f_r = 0.31$ of the available energy in product vibration and rotation, respectively. In the $v' = 0$ level the mean rotational energy is as high as 1.73 eV. The occurrence of rotational energies of this magnitude has interesting implications for the kinematic analysis of ion-molecule reactions. Here the electronic state of products is often inferred from a plateau in the plot of experimental Q values (translational endoergicities) versus collision energy by associating it with a dissociation limit.[16] If large amounts of energy are stored in rotation, limiting Q values more negative than those corresponding to the true dissociation limit will result. Observed Q plateaus can therefore only set upper bounds to dissociation limits.

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Onset of Turbulence in a Rotating Fluid*

J. P. Gollub†‡ and Harry L. Swinney
Physics Department, City College of the City University of New York, New York, New York 10031

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Light-scattering measurements of the time-dependent local radial velocity in a rotating fluid reveal three distinct transitions as the Reynolds number is increased, each of which adds a new frequency to the velocity spectrum. At a higher, sharply defined Reynolds number all discrete spectral peaks suddenly disappear. Our observations disagree with the Landau picture of the onset of turbulence, but are perhaps consistent with proposals of Ruelle and Takens.

Thirty years ago, Landau proposed[1] that the turbulent state of a fluid results from a large number of discrete transitions or bifurcations, each of which causes the velocity field to oscillate with a different frequency f_i, until for sufficiently large i the motion appears chaotic, although the time correlation functions $C(\tau)$ of the velocity field do not strictly go to zero as $\tau \to \infty$. The Landau picture has been presumed applicable to a large class of systems, including the rotating fluid that we have studied. Systems in a second class (which we will not mention further) exhibit inverted bifurcations, where the transition to turbulence is hysteretic, and usually no periodic regime precedes the onset of chaotic behavior.

The Landau picture has been challenged by Ruelle and Takens,[2] who propose on the basis of abstract mathematical arguments that the motion should be aperiodic with exponentially damped correlation functions after three or four bifurcations to time-dependent states. Recently McLaughlin and Martin[3] have performed numerical calculations on a truncated set of equations applicable to Rayleigh-Bénard convection, and they found a sharp transition to aperiodic behavior following a periodic regime, in qualitative agreement with the arguments of Ruelle and Takens.

A great variety of periodic and chaotic states have been observed in past experiments on rotating[4] and convecting[5,6] systems. These experiments have not examined the onset of aperiodicity in sufficient detail to distinguish between what we term the Landau and Ruelle-Takens pictures. In contrast, Ahlers[7] has recently observed and characterized a sharp transition to aperiodic behavior in sensitive heat-flux measurements on convecting liquid helium; however, the periodic states which presumably precede the transition were not observed.

We present here the first detailed measurements of a *local* property that shows a sequence of periodic regimes followed by a sharp and reversible transition to an aperiodic state, as de-