WOLFGANG FROBIN
CHRISTOPH SCHLIER
K. STREIN
ERNST TELOY

Ion-molecule reactions of N^+ with CO: integral reactive cross sections in the collision energy range 0.2 – 13 eV

Ion-molecule reactions of N^+ with CO: Integral reactive cross sections in the collision energy range 0.2–13 eV

W. Frobin,^{a)} Ch. Schlier, K. Strein,^{b)} and E. Teloy

Fakultät für Physik der Universität, D-7800 Freiburg, West Germany
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The guided beam technique, which allows the precise measurement of integral reactive cross sections of ions, has been used to measure the products of the collision of N^+ with CO in the energy range 0.2–20 eV (lab). All five possible ionic reaction products CO^+ , NO^+ , C^+ , CN^+ , and O^+ have been observed. The cross sections of the exothermic CO^+ and NO^+ channels show the usual decrease with E at low E (below 3 and 1 eV c.m., respectively), then increase again to a flat maximum (near 12 and 5 eV c.m., respectively). The CN^+ and O^+ channels show the expected thresholds, then a maximum (near 8 and 6 eV c.m., respectively), whereas the C^+ channel seems to have an activation energy and is still increasing at 13 eV c.m. There is no indication, in the form of kinks, of excited product channels except for dissociation. In addition, time-of-flight measurements have been done, giving some information on the forward component of the product velocity. The results are discussed in the light of simple theories, and of correlation diagrams supported by partial knowledge of the potential energy surface of $(NCO)^+$ from CI calculations by A. A. Wu. This molecule has three stable linear isomers NCO^+ , NOC^+ , and CNO^+ , which have also linear low lying excited states. So the discussion of the reaction as a collinear collision seems justified. The well in the $^3\Pi$ states can probably explain complex formation at low energies. The products CO^+ and O^+ cannot be formed adiabatically (even in C_∞ symmetry). This is in accord with the small cross section for O^+ formation, but not with the large one for CO^+ , where one has to postulate the existence of nonadiabatic surface "jumps". Additional experiments, especially differential cross sections, are needed for a more comprehensive discussion of the molecular dynamics, which, after all, is not singular but rather prototypical for triatomic chemical reactions.

I. INTRODUCTION

If one attempts to understand molecular reaction dynamics by doing experiments on the single collision level, ion-molecule reactions have some advantages over neutral ones. It is easy to follow the reactive behavior through a large energy range, and ionic products (but only those) are easily detected. Other things have been traditionally regarded as disadvantages: mass and energy discrimination of ion detectors, the difficulty to produce pure ground state ionic beams, and the dilemma of collecting reaction products completely. (This latter point is common to all beam methods.) The guided beam technique of Teloy and Gerlich¹ has to a great extent solved the problem of ground state ion beams and 4π collection geometry. Ion discrimination can be reduced to negligible factors by careful design of the mass spectrometer, and by using an electron conversion detector² of modern design to detect the ions.³

The question still remains whether ionic reactions provide us with the same insight into reaction dynamics of small (e.g., triatomic) systems as neutral ones. This has been discussed in detail, e.g., by Henschman.⁴ We tend to see even less difference between both. There has been a historical bias in neutral reactive beam work preferring reaction partners with almost closed shells like alkali or halogen atoms and molecules formed from them to those with "very open shells" like C, N, and O. As a consequence the potential energy surfaces involved in neutral reactions have been traditionally fewer and simpler than those needed to discuss ionic systems. It

is, however, the latter, more complex case which is typical for an *average* reactive system outside of organic chemistry.

In fact, one can argue that reactions of open shell atoms like C, N, and O whether ionized or not must *necessarily* involve a system of many available potential energy surfaces. The reason is that within an energy range comparable to typical reaction energies (a few eV) most of the possible reactants and products have excited states. In addition, since first row triatomics with between 18 and 22 electrons are maximally bonded, several such surfaces will have deep basins. Finally, the electron configurations of low-lying reactant states are not the same as those of low-lying states of the quasi-molecule ("collision complex"), so that configuration interaction will couple many surfaces. Therefore, as a general behavior in such very open shell reactions one will expect that atom-diatom reactions are not completely adiabatic. It is one of the motives to do experiments with such systems, to find out what the role of adiabaticity in such reactions really is.

The system $N^+ + CO$ is prototypical in yet another respect: All diatomic neutral or ionic fragments are bound. (Again this has to be expected in the middle of the rows of the periodic table.) This allows with sufficient sensitivity to observe five different reactive channels even in a triatomic reaction. As far as we know our experiment is the first complete observation of so many channels in such a simple reaction. The superiority of the beam method over most other methods in reactions with five observable branches is obvious.

In our experiment the channels

^{a)}Present address: Orthopädische Universitätsklinik, D-4400 Münster, West Germany.

^{b)}Present address: Physikalisch-Chemisches Institut der Universität, D-6900 Heidelberg, West Germany.

have been observed between 0.2 and 20 eV in the laboratory frame (0.15 to 13 eV in the c.m.). One will note that we include charge exchange [Reaction (1)] in this list, since we see no reason to use different conceptual models for rearrangement and nonrearrangement collisions.

After a description of the apparatus in Sec. II, Sec. III presents the measured integral reactive cross sections. Two further sections discuss these results in terms of simple models, with the help of our limited knowledge of the energy surfaces involved. The Appendix gives some data on forward product velocities.

II. APPARATUS

An overview of the apparatus is given in Fig. 1. It has been described in a former paper¹ so only a few remarks are necessary here. The principle of adiabatic guidance of ions by high-frequency fields has been applied three times in this machine: in the ion source (3 in Fig. 1), the mass filter (6), and the beam octopole (7).

In the *ion source* N^+ ions are produced by bombardment of N_2 with 50 eV electrons. They are stored in the rf fields and diffuse to the source exit, where they are used as a continuous stream or in pulses. The pulsed mode of the apparatus is used under one of the following conditions:

(1) to verify the de-excitation of primary ions by varying the storage time,

(2) to calibrate the energy scale by time-of-flight measurements of primary ions,

(3) to do time-of-flight energy analysis of product ions, or

(4) in those cases where the kinematics allows backward scattering of products in the laboratory frame. In this case the octopole entrance will be closed by a voltage pulse at that time, when backward scattered ions would leave the octopole in the wrong direction, reflecting those ions forward and thus into the detector.

The ion beam leaving the source contains N^+ and N_2^+ in a 3:1 ratio, after optimizing the source conditions.

Therefore, a further mass selector is necessary. We employ the rf-mass filter, which is described in Ref.

1. After passing it the contamination of the ion beam is reduced to 0.3% $^{15}\text{N}^+$, 0.12% ($\text{O}^+ + \text{CH}^+ + \text{H}_2\text{O}^+$), 0.1% N_2^+ , and less than 0.1% N_2^{2+} (estimated from $^{15}\text{N}^{14}\text{N}^{2+}$).

In addition to other chemical species one also must be careful of excited metastable species if meaningful experiments shall be done. In the case of N^+ the ^3P ground state could be contaminated by ^1D (1.89 eV, 250 s) or ^1S (4.04 eV, 0.92 s, data after Ref. 5) ions.

A careful measurement of the C^+ threshold (Fig. 2) with different ion storage fields shows that under normal conditions (source pressure 0.01 torr N_2 , continuous mode) about 0.5% N^{*+} is in the beam, which is de-excited completely in the pulsed mode after 3 ms of storage. In this way all cross sections presented in this paper have been checked and, when necessary, corrected to display pure $\text{N}^+(^3\text{P})$ cross sections. The energy spread of the ion beam has been measured by both retarding field and time-of-flight methods to be 0.15 eV FWHM (cf. Ref. 1). Time of flight allowed also us to establish the energy scale of the apparatus independent of contact potentials.

FIG. 1. Simplified scheme of the apparatus (not to scale). [1(a), (b)] Gas inlets for ion source and scattering chamber; [2(a), (b)] to cold traps and mercury diffusion pumps; (3) storage ion source; (4) cathode and electron beam; (5) electrodes for shaping and pulsing of the ion beam; (6) rf mass and velocity filter (8 cm long); (7) rf octopole (38.7 cm long, free diameter 0.52 cm); (8) scattering chamber (effective length 9.1 cm); (9) ionization gage; (10) capacitance manometer; (11) vent for the scattering chamber, operated by an electromagnet; (12) acceleration lens; (13) lenses for the shaping of the ion beam; (14) entrance slit of the mass spectrometer (0.15×1.4 cm); (15) metal box, defining the electrical potential in the mass spectrometer (−3 kV); (16) poles of the 90° magnet (radius 12.5 cm); (17) exit slit (0.3×1.4 cm); (18) voltage feed through and converter (−30 kV); (19) scintillator and quartz window; (20) photomultiplier (Valvo 56 DVP-03).

FIG. 2. Threshold behavior of the C^+ channel with (▲) and without (●) contamination of the N^+ beam with metastables.

After leaving the mass filter the ions are guided by a rf octopole which extends through the scattering chamber. The latter contained CO gas at 295 K and at a pressure of about 10^{-4} torr measured by a capacitance manometer. Checking several such manometers of different manufacturers against each other leads us to believe that the error of pressure determination is no more than 5%. The scattering chamber has a magnetically operated vent, which allows one to vary the chamber pressure by a factor of 10 without changing the background pressure appreciably. The rf octopole serves further to collect all secondary ions scattered elastically or reactively, provided the transversal energy of those ions is less than about 2 eV, which is the maximum effective potential produced by the inhomogeneous rf fields. This means that, at least at low energies, our apparatus performs true 4π ion collection, which is a problem in all other ion beam machines (except merging beams, but they have their own problems). Even backward scattered ions are included in the cross sections, as has been described above.

The ion collection efficiency together with the transmission to the detector has been checked by comparing the sum of all ion production cross sections with the ion loss cross section derived from the attenuation of the primary beam. Table I shows that below 6 eV (lab.) the two values coincide to within their reproducibility of 2%–3%. At higher energies some ions are lost, and the amount increases with energy to about 15% at 20 eV (lab.). From our experience with Ne^+-Ne charge transfer collisions, where a similar loss occurred,⁶ we believe that this loss comes mainly from large angle elastic scattering of the primary beam. Therefore, the effect will probably not influence the measured branching ratios. The ions are detected by a magnetic mass spectrometer followed by a scintillation detector.² The latter is a large improvement to particle multipliers: Ion counting losses are now of the order of a few percent,

TABLE I. Effective cross sections ($\text{\AA}^2$) as a function of laboratory energy (eV). Q_E is the cross section from attenuation of the primary beam.

E_{lab}	Q_{CO^+}	Q_{NO^+}	Q_{C^+}	Q_{CN^+}	Q_{C^+}	Q_E
0.2	28.3	2.58				
0.25	22.4	2.27				
0.30	18.6	1.99				
0.35	15.8	1.75				
0.40	13.6	1.55				
0.45	11.7	1.41				
0.50	10.4	1.30				
0.60	8.4 ₅	1.09				9.6
0.70	7.24	0.94				
0.80	6.28	0.81				
0.90	5.47	0.72				
1.00	4.80	0.63 ₅				5.4
1.1	4.37	0.59				
1.2	3.96	0.53				
1.3	3.64	0.49				
1.4	3.38	0.46				
1.5	3.21	0.44				
1.6	3.10	0.42	0.0006			
1.7	2.96	0.40 ₅	0.0008			
1.9	2.81	0.40	0.0015			
2.1	2.68	0.39 ₅	0.002			
2.3	2.54	0.40	0.003			
2.5	2.42	0.42	0.007			
2.8	2.29	0.48	0.012			
3.1	2.19	0.59	0.021			2.7 ₅
3.4	2.09	0.69	0.033		0.0015	
3.7	2.04	0.78	0.053	0.0015	0.0035	
4.0	1.99	0.85 ₅	0.081	0.007	0.008	
4.3	1.95 ₅	0.92	0.113	0.023	0.015	
4.6	1.96	0.97	0.153	0.044	0.023	
4.9	1.95	0.99 ₅	0.198	0.094	0.031	3.3
5.2	1.97	1.01	0.248	0.148	0.042	
5.5	1.99	1.02	0.297	0.213	0.052	
5.8	2.01	1.02 ₅	0.345	0.282	0.063	
6.1	2.03 ₅	1.03	0.395	0.345	0.074	3.9
6.4	2.07	1.03 ₂	0.439	0.412	0.084	
6.7	2.10	1.03 ₂	0.482	0.473	0.094	
7.0	2.14	1.03	0.52	0.54	0.103	
7.5	2.22	1.02	0.58 ₅	0.62	0.108	
8.0	2.29	1.01	0.63 ₅	0.68 ₅	0.109 ₅	5.1
8.5	2.37	0.99	0.66	0.74	0.110	
9.0	2.46	0.97	0.68	0.78	0.110	
9.5	2.54	0.95	0.69 ₅	0.80 ₅	0.108 ₅	
10.0	2.64	0.92	0.70 ₅	0.82 ₅	0.106	5.6 ₅
10.5	2.73	0.89	0.71 ₅	0.83 ₅	0.104	
11.0	2.83	0.86	0.73	0.84 ₅	0.101	
11.5	2.92	0.81 ₅	0.75	0.85	0.098	
12.0	3.02	0.76	0.79	0.84 ₅	0.094 ₅	6.1
12.5	3.10	0.70	0.85	0.83 ₅	0.090 ₅	
13.0	3.16	0.65	0.93	0.82	0.086	
13.5	3.21	0.60	1.01	0.80	0.081	
14.0	3.25 ₅	0.56	1.09	0.77	0.077	6.5
14.5	3.28	0.51 ₅	1.16 ₅	0.73 ₅	0.074	
15.0	3.30	0.47 ₅	1.24 ₅	0.70 ₅	0.071 ₅	
15.5	3.32	0.43	1.32	0.67 ₅	0.069	
16.0	3.34	0.39	1.39	0.64	0.067	6.7
16.5	3.35	0.35 ₅	1.45	0.61	0.065 ₅	
17.0	3.36	0.32	1.51 ₅	0.57 ₅	0.064	
17.5	3.36 ₅	0.29	1.57	0.54	0.063	
18.0	3.37	0.26	1.62 ₅	0.51	0.061 ₅	6.9
18.5	3.37	0.24	1.67	0.47 ₅	0.060	
19.0	3.36	0.21 ₅	1.71 ₅	0.45	0.059	
19.5	3.35 ₅	0.19 ₅	1.76	0.43	0.058	
20.0	3.34 ₅	0.17 ₅	1.80	0.41	0.057	6.9 ₅

and their values can be deduced from the pulse height distributions.³ For this experiment counting losses for the different species have not been determined; the charge balance mentioned above shows, however, that discrimination is very small. Counting losses from scaler dead time have been corrected for in the usual manner.

All our measurements were performed as a function of beam energy by automatic stepping control electronics. One cross section function was measured in about 2 h, and all have been measured several times on different days. They were reproduced within 2%–3%.

In addition, time-of-flight measurements were performed by pulsing the octopole entrance (pulse width typically 1 μ s) and counting the ions in a multiscaler with small channel dwell time.⁷ For the primary beam this procedure serves to check the energy scale, which was found to be within 20 mV of the retarding field value. For secondary ions things are not as simple, since they are produced under unknown angles and guided by reflections at the "walls" of the octopole field. Therefore, one measures only the velocity component along the axis of the octopole (forward scattering direction), or, otherwise stated, a certain combination of E' and ϑ' .

III. RESULTS AND DISCUSSION OF ERRORS

Reaction cross sections for Reactions (1)–(5) plus the absorption cross section of N^+ in CO are plotted in Fig. 3 and presented with higher accuracy in Table I. These are still effective cross sections i. e., convoluted with

FIG. 4. Threshold of endothermic channels. The points are measured. Straight lines are drawn under the assumption of a linear threshold law; their convolution with target motion fits the measured points for CN^+ and O^+ but not for C^+ , where the arrow gives the thermodynamic threshold value.

the beam width (0.15 eV) and "Doppler" broadening from the target gas motion. The latter has a half-width of $\Delta E_{1/2} \approx (0.1 E_{c.m.})^{1/2}$ increasing from 0.15 at $E = 0.2$ to 1.15 at $E = 13$ eV. Since the cross sections show no narrow structures, the deconvoluted curves would not look much different from those in Fig. 3 except at the thresholds of endothermic channels. These thresholds are displayed with high resolution in Fig. 4. The O^+ and CN^+ curves can obviously be represented by a linear threshold law convoluted with the apparatus resolution, which is not the case for C^+ .

Points in Figs. 2 and 4 are single, not smoothed measurements, and can serve to show the statistical accuracy of the data. Systematic errors of the relative cross sections are probably smaller than 5%, and those of the absolute values may be as large as 10% below 6 eV (lab.) = 4 eV (c.m.) increasing to 15% at the highest energy. The energy scale is accurate to about 50 meV (cf. also the discussion of threshold energies below).

IV. DISCUSSION

A. Comparison with other experimental data

We have found three references in the literature reporting on the reaction $N^+ + CO$, but in each case data pertain only to the charge exchange channel [Reaction (1)]. Fehsenfeld *et al.*⁹ give a rate constant of $k = 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ($\pm 30\%$) at 300 K measured with a flowing afterglow apparatus. Comparison can best be done by computing $k^* = \sigma(v_1) \times v_1$ from the beam data¹ (where v_1 is the beam velocity), since k^* but not σ_{eff} will have a finite limit for $v_1 \rightarrow 0$. At our lowest energy of 0.2 eV (lab.) k^* is $4.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is gratifying, though perhaps fortuitous. Similarly, an extrapolation of our k^* values between 0.2 and 0.35 eV leads to a value of 7

FIG. 3. Integral cross sections (log scale). Σ is the sum of the observed channels. The arrows give the position of dissociation thresholds into three atoms.

$\times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ to be compared with Fehsenfeld *et al.* In view of the errors of both experiments this can be considered good agreement.

The second comparable experiment has been done by Rutherford and Vroom¹⁰ with a tandem mass spectrometer. Their cross section for Reaction (1) is about half as large as ours. This may be due to uncertainties in the collection efficiency of such a machine, especially if the products to be collected have large angles as our time-of-flight results suggest.

Finally, Hasted¹¹ has performed swarm experiments for $\text{N}^+ + \text{CO}$ in the energy range 0.05 to 1 eV (c.m.). Our data are in rough agreement with his results for Reaction (1), i.e., CO^+ , but are a factor of 3 to 6 lower than his lower limit for Reaction (2). Here the interpretation of Ref. 11 seems erroneous. Since the reaction $\text{NO}^+ + \text{CO} \rightarrow \text{CO}^+$ is endothermic by 4.75 eV, it will play no role in the drift tube, and σ_{23} of Ref. 11 vanishes. The lower limit for k_{12} [Eq. (23) of Ref. 11(b)], however, holds only if $\sigma_{13} < \sigma_{23}$. A meaningful comparison thus has to expect a reinterpretation of the drift tube data.

At this point it may also be appropriate to discuss the values of our threshold energies. Comparison with literature data is hampered for the CN^+ and O^+ channels by the uncertainty of the values of the dissociation and ionization energies of CN. Taking both values from Dibeler and Liston¹² the expected thresholds are $\text{CN}^+ - 2.87$ eV and $\text{O}^+ - 2.28$ eV, while the data of Berkowitz *et al.*¹³ give 2.91 and 2.49 eV, respectively. Since the latter values have been obtained more directly, we prefer these; moreover, our measured thresholds (deconvoluted) of 2.90 and 2.61 ± 0.10 eV, respectively, support strongly the lower values of D_0 and I.P. (Two other papers give values only for D_0 , one¹⁴ supporting the low, one¹⁵ the high value, both use rather indirect methods.) Turning things around, if we assume no activation energies, our threshold measurements give $D_0(\text{CN}) = 7.58 \pm 0.10$ eV, $\Delta H_f^0(\text{CN}) = 106.5 \pm 2$ kcal/mole, and I.P. (CN) = 13.9 ± 0.2 eV. The threshold for C^+ production (corrected for target gas motion) is 1.33 ± 0.10 eV, in accord with the value of 1.35 eV derived from literature data. However (cf. Fig. 4), the linear rise of the cross section extrapolates to a higher threshold of $2.23_{-0.20}^{+0.10}$ eV. This is further discussed in terms of a possible activation barrier in Sec. V below.

B. Comparison with simple theoretical models

The simplest class of theoretical models, with which we may compare our cross sections, are those which use only the long-range part of the intermolecular potential to compute a "capture" cross section, which is then identified with a reactive cross section. The uncritical use of this Langevin (–Gioumoussis–Stevenson¹⁶) theory and its elaborations, e.g., average quadrupole orientation (AQO),¹⁷ has been rightly blamed by Henschman,¹⁸ and our results give but another example of its inadequacy for computing reactive or charge exchange cross sections at collision energies higher than thermal.

Nevertheless, it is worthwhile to discuss the long range potential $V(R, \theta)$ of $\text{N}^+ - \text{CO}$. It can be written

$$V(R, \theta) = -\frac{q \cdot \mu}{R^2} \cos \theta + \frac{q \cdot Q}{R^3} P_2(\cos \theta) - \frac{q^2 \bar{\alpha}}{2R^4} \left[1 - \frac{2}{3} \frac{\alpha_{\parallel} - \alpha_{\perp}}{\bar{\alpha}} P_2(\cos \theta) \right], \quad (6)$$

where q is the charge of N^+ and μ , α , Q are the dipole moment (0.112 D^{19}), polarizability tensor ($\bar{\alpha} = 1.94 \text{ \AA}^3$, $\alpha_{\parallel} - \alpha_{\perp} = 0.52 \text{ \AA}^3^{20}$), and quadrupole moment ($Q \approx 2.4 \times 10^{-26} \text{ esu cm}^2^{21}$) of CO, respectively. Of the four terms in Eq. (6) the first (μ) and fourth ($\alpha_{\parallel} - \alpha_{\perp}$) are negligible, and the other two are comparable at distances of interest. They add for collinear orientation of $\text{N}^+ - \text{CO}$, and compensate largely down to $R \sim 5a_0$ for 90° orientation, giving some preference to collinear collisions as discussed below.

The computed capture cross sections are $23.5 E^{-1/2} \text{ \AA}^2 (\text{eV})^{1/2}$ with the $\bar{\alpha}$ term only, and $23.1 E^{-2/3} \text{ \AA}^2 (\text{eV})^{2/3}$ in the 0° -locked quadrupole case. AQO theory would give a small correction to the polarization-only formula. Our result for the sum of all channels (i.e., all ionic products except scattered N^+) gives $\sigma_{\text{sum}} \sim E^{-1}$ and falls short of both the above approximations by a factor of 2 even at our lowest energy (0.13 eV c.m.). This behavior is not uncommon (e.g., Refs. 22–24), and is consistent with Henschman's view.

While the foregoing model is limited at most to predict an upper bound to σ_{sum} , statistical models foretell mainly branching ratios. One such model is phase space theory as developed by Pechukas and Light.²⁵ Not all data required as an input for this theory are available: Polarization values of excited states must be guessed, and the usual treatment assumes a pure polarization potential in the incoming and outgoing channel. Furthermore, it is not clear which electronic states have to be included, e.g., should one count spin-forbidden reactions? The phase space prediction has been computed by one of us (K.S.²⁶). It shows some trends of the experiment (thresholds, decreasing cross section for exothermic channels), which, in fact, are already included in the input of the model. But Fig. 5 shows also that most detail of the prediction is wrong even at low energies. This is also true if one computes branching ratios only, or even if one adds two pairs of charge-exchanged channels to study whether rearrangement might be statistical even if charge exchange is not {i.e., even $[\sigma(\text{O}^+) + \sigma(\text{CN}^+)] / [\sigma(\text{C}^+) + \sigma(\text{NO}^+)]$ is not well predicted}. Finally, also the threshold behavior of endothermic channels is not brought out by phase space theory except for CN^+ : The steepness of threshold for O^+ is wrong, and the slow onset of the C^+ threshold is, of course, not predicted.

Again, as with the former "theory," one can argue that there is no reason to expect phase space theory in this simple form to hold for our experiment. But this is an argument counter to the spirit of such simple theories: They are put forward not because one expects them to hold very well but because they are simple, and it is one of the tasks of experiment to check how far they hold even if their underlying assumptions are not strictly true.

The third "simple theory," which we can test against

FIG. 5. Prediction of phase space theory. L. G. S. is the Langevin cross section.

our data, is the "information theoretic" approach of Levine and Bernstein.²⁷ Here, the underlying assumption is that "molecular chaos" is not only valid for equilibrium of a large number of molecules, but also—with some constraints, which have to be found out—for the state distribution of the products of a single collision.

It may be worthwhile to remark that the invocation of information theory at this point is misleading, and can sometimes bar the understanding of this type of statistical theory. The outcome of physical experiments cannot—after the experiment has been set up—depend on information. Of course, the experimenter may choose to make *his expectation* of the outcome depend in a certain way on information. He may for example postulate that he will expect the outcome as random as possible under *known* constraints. He can then use information theory to define randomness, and this is the *only* connection of information theory (a theory about communication) with statistical mechanics (a theory about the physical world). We have good reason not to confound two theories with such different universes of discourse.

In the Bernstein-Levine approach the relative probabilities for the channels of an $A + BC$ collision are²⁸

$$P_k^0 \sim g_k \mu_k^{3/2} (\omega_k B_k)^{-1} E_k^{5/2}, \quad (7)$$

where g_k is the statistical weight of the electronic product state k , μ_k , ω_k , and B_k are the reduced mass and vibration and rotation constants of the product molecule, respectively, and $E_k = E - \Delta E_{k0}$ is the available c.m. en-

ergy. In deriving Eq. (7) the rigid rotor harmonic oscillator approximation has been made.

Since the diatomic products of our reactions are very alike, the main factors in Eq. (7) are the weight g_k and the energy factor $E_k^{5/2}$. The latter will tend to be equal for all channels at large enough E .

Figure 6 shows some of the possible branching ratios

FIG. 6. Unconstrained prior branching ratios compared with measured ones. Note that the scale is logarithmic

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FIG. 8. Adiabatic correlation diagram ($C_{\infty v}$ symmetry) for the NOC^+ isomer. The energies of the bound conformation have been guessed, and a few states have been left out.

form of a kink in the cross section curves, though the noise of the data is very low. This is in complete agreement with observations of chemiluminescence under single collision conditions: In those few cases where absolute cross sections are given³⁹⁻⁴² they are at most a few percent of the total reaction cross section.

Let us therefore see how far we can understand the measured cross sections by assuming pure adiabaticity, i.e., no surface hopping. In this case the correlation diagrams show the available states in every arrangement channel. The reactants start on the $1^3\Pi$ or $2^3\Sigma^-$ surface ($1^3A'$, $2^3A''$, and $3^3A''$ in C_s symmetry). We find that *under both symmetries* NO^+ , CN^+ , and C^+ can be formed adiabatically but O^+ and CO^+ cannot.

The O^+ channel [Reaction (4)] shows the expected behavior; it is 10 times weaker than the allowed channels. Since the $1^3\Sigma^-$ and $2^3\Sigma^-$ surfaces are asymptotically 0.5 eV apart, and probably some pseudocrossing comes into play (see below), a "hopping probability" of 1/10 seems not unreasonable.

The situation is different, however, for CO^+ , the charge exchange channel: Though adiabatically forbidden it is from 11 (at 0.2 eV lab.) to 2 (at 5 eV) to 19 (at 20 eV) times stronger than the NO^+ channel, and everywhere stronger than the total rearrangement. Moreover, the lack of NO^+ data from the afterglow indicates that Reaction (1) is much faster than (2) even at thermal ener-

gies, in accord with the trend of our data. There is some tradition in the literature (e.g., Ref. 43) to treat charge exchange (without rearrangement) on a completely different footing than rearrangement (with or without charge exchange), but if we want a unified conceptional model (semiclassical, to be sure) we cannot single out charge exchange from the other processes. In such a model we have to search for regions of conformation space in which either localized ("Landau-Zener") or delocalized ("Demkov") pseudocrossings facilitate the "jump" from $2^3\Sigma^-$ or $1^3\Pi$ to $1^3\Sigma^-$ or $1^5\Sigma^-$. The latter type may well be similar to that "direct" electron exchange, which one traditionally computes (e.g., Ref. 44), even if the shape of our cross section is different from that of the simple theory.⁴⁴ In any case, if we discuss correlation diagrams for molecular states, we have to find *diabatic* correlations now in addition to the adiabatic ones.

Postponing this question until Sec. V let us discuss first the behavior of the cross sections. It is striking that the exothermic channels show a minimum between the large low energy cross section and the flat peak in the eV range. This behavior is not uncommon, and Ferguson²² remarks that it is found generally in reactions where the cross section is well below the Langevin limit. An explanation in terms of hopping probabilities is put forward by Hasted,¹¹ but since the NO^+ production is adiabatically allowed, this cannot be the whole truth. The most straightforward interpretation ascribes the low energy part of the cross section to capture in an attractive potential, and the medium energy part to a direct collision as one gets for endothermic channels. In this case one could understand why a large capture cross section leads to no minimum: If the direct part of the cross section is fixed at a small value and the capture part increased, the minimum will disappear.

If we talk of capture, we do not mean that the asymptotic long range potential is the one to provide capture at our energies. At 1 eV the Langevin critical radius is $\sim 5a_0$, and the long range potential is invalid there. Also, we do not mean that capture must lead to reaction with high probability. From our limited knowledge of the $(\text{CNO})^+$ surfaces we feel that the weak attractive well of the $1^3\Pi$ state (Wu's calculations³³ give a well depth of 0.38 eV at 4.6 a_0 for the NCO^+ isomer) is the most probable candidate to explain the low energy behavior of the NO^+ cross section. Since the potential is not $\sim r^{-4}$, it is no wonder that the energy dependence is not $\sim E^{-1/2}$. For CO^+ in addition to the attractive well in the input channel a mechanism must be found which transfers to the surface of the output channel. In a long lived capture complex, however, this transfer must not be one with high probability per passage of a pseudocrossing, as Zahr and Miller⁴⁵ have shown in a similar case. So the rotational coupling from $1^3\Pi_2$ to $1^3\Sigma_2^-$ or even the spin-orbit coupling of $1^3\Pi_2$ to $1^5\Sigma_2^-$ might suffice to produce the effect. Further data on the surfaces, including the NOC^+ isomer, are needed to say more.

The only additional resolved structure in the cross section vs energy are the "kinks" in the C^+ and O^+ channels at 7.7 ± 0.3 and 9.8 ± 0.8 eV (c.m.), respectively.

FIG. 9. Schematic diagram of avoided crossings of potential energy surfaces (a) by configuration interaction and (b) by LS coupling. Thin lines: diabatic behavior in our nomenclature.

These energies coincide with those of dissociation channels

The time-of-flight spectra for C^+ and CO^+ show that near $E = 7.5 \text{ eV}$ (c. m.) these products have larger mean angles and/or smaller product energies than at other energies. This is not the case for CN^+ . Moreover, the sum of $\text{C}^+ + \text{CO}^+$ will still give a smooth curve, while this is not the case for $\text{C}^+ + \text{CN}^+$. We conclude, therefore, that dissociation of CO^+ is mainly observed. The dissociation of CO^+ along its vibrational coordinate into ground state C^+ and O is adiabatically allowed.

The situation is not so clear for the additional O^+ observed, since the amount is so small on an absolute scale, and the time-of-flight experiments are inconclusive. However, the dissociation of CO^+ into $\text{C} + \text{O}^+$ is not very probable on adiabaticity grounds. On the other hand, $\text{N} + \text{O}^+$ in their ground states are the normal dissociation products of NO^+ , so we observe probably the dissociation of that molecule in the final phase of the collision.

V. CAN WE PREDICT DIABATIC CORRELATIONS?

The discussion on the CO^+ channel has shown that the understanding of collision dynamics in multisurface collisions cannot proceed without some knowledge on inter-surface coupling. It is therefore important to predict in which parts of conformation space such couplings occur. This is the more so, since, even if quantum chemists should become more used to computing coupling matrix elements, one would not like to compute every sys-

tem which one wants to discuss. Instead, qualitative predictions, be it from analogies with electronically similar molecules, are needed.

It is out belief that such prediction can be done. The following is an attempt in this direction: Similar ideas have been promoted.⁴⁶ Let us first recognize that what we usually call an adiabatic surface is only adiabatic, i. e., does *not* cross, with respect to configuration interaction (cf. Fig. 9), but crosses, i. e., should be called diabatic, with respect to LS interaction. This shows that if one frees the concept of an adiabatic surface from its very specialized notion in the context of the Born-Oppenheimer approximation, "adiabatic" and "diabatic" behavior are concepts *relative to each other* only. "Switching on" a new interaction renders a surface, which was diabatic and crossed at certain points, into an adiabatic one with an "avoided crossing." The same happens when some symmetry is reduced, turning a good quantum number into one no longer "good."

The quantum numbers which are connected with the introduction of configuration interaction, thus producing adiabatic behavior in the traditional sense, are the occupation numbers of orbitals defining the "electron configuration" of a molecular state. In the SCF approximation such a configuration is always defined, even if one needs several configuration functions to describe a multiplet state. In a theory lacking spin-orbit coupling even the energy of a configuration would be well defined in each case. In simple cases it is well known that at a pseudocrossing the adiabatic state changes its configuration, e. g., in LiF . Coming from infinite R the ground state is $\text{Li}(\sigma^2\sigma)\text{F}(\sigma^2\sigma^2\pi^4\sigma)^1\Sigma^+$ with two nonequivalent σ orbitals singly occupied, but it changes to $\sigma^2\sigma^2\sigma^2\pi^4\sigma^2$ (which is the asymptotic configuration of $\text{Li}^+ - \text{F}^-$) at the famous crossing of ionic and covalent states.

Let us apply this treatment to NCO^+ . At infinite $R_{\text{N-CO}^+}$ the ground state is $\text{N}(^4S)\pi^2\sigma - \text{CO}^+(^1\Sigma^+)\pi^4\sigma$, giving a molecular configuration $\pi^4\sigma\pi^2\sigma$ with states $^3\Sigma^-$ and $^5\Sigma^-$. This configuration does not connect diabatically to the ground configuration of bound NCO^+ , which is $\pi^4\sigma^2\pi^2$, but to a highly excited state of the molecule. Actually, it follows from Wu's calculations³³ that $\pi^4\sigma\pi^2\sigma$ is the main configuration of the second $^5\Sigma^-$ state and not less than the fourth $^3\Sigma^-$ state at distances near the molecular equilibrium ($R_{\text{NC}} = 2.6a_0$, $R_{\text{CO}} = 2.2a_0$). On the other hand, the ground state of the bound molecule $^3\Sigma^-$ belongs to the configuration $\pi^4\sigma^2\pi^2$, which dissociates diabatically into $\text{N}(^3P)\pi^2$ and $\text{CO}(^1\Sigma^+)\pi^4\sigma^2$, which form the second $^3\Sigma^-$ state of the dissociated arrangement. (Other states of the configuration $\pi^4\sigma^2\pi^2$ are $^1\Delta$, which is $1^1\Delta$ at equilibrium, but is connected diabatically to $2^1\Delta$ at dissociation, and $1^1\Sigma^+$ at equilibrium becoming a mixture of $1^1\Sigma^+$ and $3^1\Sigma^+$ at dissociation.) From the said behavior we conclude, though not with mathematical rigor, that the two lowest $^3\Sigma^-$ states of the NCO^+ molecule cross diabatically and therefore must adiabatically have an avoided crossing when R_{NC} goes from $\sim 2.6a_0$ to infinity. The CI calculations show that this crossing is not very well born out in the energy curves, which are practically parallel with 0.5 eV distance from $R_{\text{NC}} = \infty$ down to $\sim 7a_0$, and then diverge. However, the calculations show as well that

FIG. 10. Results of time-of-flight measurements of forward product velocities for, (a) CN^+ , (b) CO^+ , and (c) C^+ . Points are measured arrival times; see text for method of plotting and comparison with computed curves. The arrow in the C^+ channel gives the threshold energy for dissociation.

the main configurations of states $1^3\Sigma^-$ and $2^3\Sigma^-$ are swapped between 7 and $4a_0$, such that a matrix element of $\partial/\partial R$ of the order of $(3a_0)^{-1}$ can be expected to couple the pair of surfaces.

A similar situation pertains to almost all states of NCO^+ : The low-lying configurations of dissociated reactants or products are high lying at short distances and *vice versa*. This is a consequence of the strong open shell character of the constituents (atoms or diatoms). A similar behavior must therefore be expected in other cases of molecule formation from C, N, O, and their

diatoms and hydrides. It is important to note that this situation has nothing to do with the fact that we treat ionic rather than neutral systems here.

The mechanism just discussed couples the surfaces on a locus which is principally across the reaction coordinate. There are at least three other ways of coupling (cf. also Refs. 47 and 48). A surface pseudocrossing parallel to the entrance or exit valley of a reaction can be expected if the diatomic potential curves of BC and BC^+ (or BC and BC^* for that matter), properly shifted to the energies of the $\text{A}^+ + \text{BC}$ system, cross. The pro-

tototype of this type of crossing, where vibrational, not translational, energy is needed to produce the surface hop, is H_3^+ .⁴⁹ Here a "seam" connects the two lower $1\Sigma^+$ surfaces, which is parallel to the bottom of entrance and exit valley for $\text{H}^+ + \text{H}_2$ from infinity down to $5a_0$, where it dissolves. We have checked that this kind of crossing is not found between the entrance channel $\text{N}^+ - \text{CO}$ and the charge exchange channel $\text{N} - \text{CO}^+$, neither at $R_{\text{NC}} = \infty$ nor at $R_{\text{NC}} = 5a_0$.

Another possibility is crossing in a bent conformation, leaving a pseudocrossing as a remnant in the collinear conformation. For our system, since all interesting states have been calculated to be linear, it is improbable that bent conformations play a large role. Finally, spin-orbit coupling should not be completely forgotten. Generally, diabatic passage through crossings of different spin states is assumed, but there are few hard experimental proofs. Taking known spin-orbit splittings as an estimate for the coupling (50 cm^{-1}) we compute a "jumping" probability [adiabatic behavior in our sense, see Fig. 9(b)] of about 0.3% per crossing. (We assume $E = 1 \text{ eV}$, masses of $\text{N}^+ - \text{CO}$, typical $H'_{11} - H'_{22}$ of $1 \text{ eV}/a_0$.) Therefore, in long lived intermediate complexes spin-orbit coupling may well be a means of jumping from "one surface" to the "other."

VI. CONCLUSION AND ACKNOWLEDGMENTS

The interpretation of our measurements of $\text{N}^+ + \text{CO}$ leaves more questions open than answered. Some of these can be answered with more experiments (the measurement of $d^2\sigma/d\Omega dE'$ is planned, and similarly for that of the $\text{C}^+ + \text{NO}$ reactions). Others have to await more calculations, and the foregoing discussion shows what to calculate. Additional data could be provided by a search for product (chemi-)luminescence.

On the other hand, the discussion shows that much has to be done to really understand an average triatomic reaction as ours is. We regard our data as a first step in this direction.

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APPENDIX: TIME-OF-FLIGHT RESULTS

As mentioned at the end of Sec. II ion flight times can be measured in our apparatus. They can be used to compute forward velocities of product ions (i.e., $v'_z = v' \cos\theta'$ in the laboratory frame). A few exploratory experiments of this kind have been done. The results are plotted in Fig. 10 as $t \times (E_{\text{lab}})^{1/2}$, where t is the time difference between the arrival times of primary and secondary ions. The dotted curves display for the indicated scattering angles the values of $t \times E^{1/2}$ which one computes provided the products are not internally excited or, otherwise stated, $\cos\theta'$ is equal to $\cos\theta'_{\text{true}} \times (1 - \beta)^{1/2}$, where β is the fraction of available energy transferred into internal excitation. Since we measure only the for-

ward velocity component, a large t means either a low product energy or a large product angle. To be more specific a Newton diagram shows that at a certain t (i.e., v'_{lab}) a limited range of product translational energies can contribute. A large inelasticity must always give times of flight near the curve marked 90° ; on the other hand, if $t = t(90^\circ)$, the scattering angle is 90° c.m. independent of E' .

Figure 10 gives three examples. CN^+ shows moderate production angles and inelasticities. CO^+ , on the other hand, is produced at large angles (and with unknown excitation) for beam energies $\geq 5 \text{ eV}$. Finally, C^+ shows a peaked behavior (near the threshold for $\text{C}^+ + \text{N} + \text{O}$), where either the production angle is increased or (more probably) the internal excitation of NO increases sharply.

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