AIP | The Journal of Chemical Physics

Cross Section for Atom Exchange with Charge Transfer in a Molecular Collision

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Citation: The Journal of Chemical Physics **44**, 2540 (1966); doi: 10.1063/1.1727086
View online: http://dx.doi.org/10.1063/1.1727086
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/44/6?ver=pdfcov
Published by the AIP Publishing

volving vibrational transition multipole moments. Because the vibrational exciton bandwidth is expected to be of the order of 1 cm^{-1}, an efficient channel for vibrational relaxation in the crystal is available. Anharmonicity effects in large polyatomic aromatic molecules, where many atoms are involved in the normal vibrations, are usually extremely small[6] and will not lead to a mismatch of the energy levels.

Consider the case of crystalline anthracene. Provided that the vibrational exciton bandwidth I is large relative to β_n, the rate of transfer of vibrational energy may be shown to be[2,7] $\mathcal{R}=\beta_{\mathrm{el}}F/\hbar I$. The necessary Franck–Condon factors may be computed after the vibrational overlaps for skeletal stretching, CH stretching, and carbon-atom and CH out-of-plane bending motions are evaluated. Using $\beta_{\mathrm{el}}\approx 0.01\ \mathrm{cm}^{-1}$, and computing $I\approx 0.2\ \mathrm{cm}^{-1}$ for the quadrupole coupled vibrational exciton band, we find[8]

$$\mathcal{R}\approx 10^2\ \mathrm{sec}^{-1}$$

which leads to a predicted triplet lifetime of 10 msec, in fortuitous agreement with experiment. The quoted value of $\mathcal{R}$ is uncertain to an order of magnitude (possibly two), but is still reliable enough, in our opinion, to show that the nature of the coupling of the hot molecule to the medium may play an important role in determining the rate of a radiationless transition.[9]

Putting aside quantitative details, what qualitative predictions can be made? First, the coupling of a vibrationally hot molecule to a glassy medium is smaller than the corresponding coupling in the pure crystal because, when the matrix is of different species from the hot molecule, resonant transfer of energy does not occur. Second, it is important that the vibrational energy be removed by free-running excitons because (a) a lattice deformation tends to decrease I greatly, (b) in the new quasistationary state of molecule plus deformed medium, β_{el} may be altered by mixing in of new states, (c) when I is not much greater than β_n, the analysis leading to the rate equation cited is no longer valid with the result that a single vibronic state is not coupled to a band of host vibrational states.

In view of the preceding comments, it would be interesting to know if the lifetime of the triplet of 2,2-paracyclophane differs much between EPA glass and pure crystal. Our analysis leads to the prediction that it should not, since this compound forms an internal triplet excimer[10] and the crystal structure is such that there ought to be a very small vibrational bandwidth. Indeed, we are led to suggest, on the same grounds, that the triplet of crystalline [2,2-] paracyclophane may be long lived relative to the triplet of crystalline benzene.

We conclude that the assumption that I is always sufficiently large that the rate-determining step in a radiationless transition is the tunneling between potential-energy surfaces is not, *a priori*, justified. Indeed, there seem to be cases where the experimental data require a different interpretation.

It is, of course, possible that β_{el} is not independent of the surrounding medium, and that the approximation of writing β_n as a product is not sufficiently accurate because of changes in coupling in the highly excited vibrational states. The magnitudes of these effects remain to be explored.

We wish to thank the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and the U. S. Public Health Service for financial support. We have also benefited from the use of facilities provided by the Advanced Research Projects Agency for materials research at the University of Chicago.

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[6] In the case of the $\mathfrak{a}_{1g}$ vibration of benzene, the anharmonicity factor is about 0.5 cm^{-1} [F. M. Garforth and C. K. Ingold, J. Chem. Soc. (London) **1948**, 417]. The anharmonicity factors for naphthalene and anthracene are expected to be smaller.

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[8] The estimate for β_{el} comes from Ref. 2. To compute the vibrational overlap integrals, the method of E. F. McCoy and I. G. Ross [Australian J. Chem. **15**, 573 (1962)] was used to estimate changes in the origins of the normal modes in the excited state. E. Hutchisson's formula was then used [Phys. Rev. **36**, 410 (1930)]. Normal mode frequency changes in the excited state were estimated from experimental data on analogous systems, and C. Manneback's formula used to compute the overlap integrals [Physica **17**, 1001 (1951)]. The estimated vibrational bandwidth agrees with the few data available for analogous systems [e.g., T. M. Nedungadi, Proc. Indian Acad. Sci. Sec. A **15**, 376 (1942)].

[9] Pure crystals of benzene, naphthalene, and anthracene do not phosphoresce. Although this lack of phosphorescence is usually attributed to efficient triplet–triplet annihilation, examination of the data obtained in Ref. 3 shows that the biexciton annihilation process does not alter the effective lifetime of the triplet state for triplet-exciton concentrations smaller than $10^{13}\ \mathrm{cm}^{-3}$. We conclude that the decrease in the lifetime of the triplet state arises from an efficient monomolecular decay process, in agreement with the arguments we have advanced.

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Cross Section for Atom Exchange with Charge Transfer in a Molecular Collision[*]

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(Received 17 November 1965)

A MOLECULAR beam has been used to study the exchange reaction

$$N_2+CO\rightarrow NO^{+}+CN^{-}, \tag{1}$$

from threshold (11.9 eV) to 60 eV. The absolute cross section was determined by total negative-ion collection, and a mass spectrometer was used to monitor the NO^{+} ions.

Fast neutral beams of N_2 and CO were produced[1] by electron-impact ionization, electrostatic acceleration, and neutralization by resonant charge transfer. These beams impacted on CO and N_2 thin gas targets.

Two types of measurement were made. The first[2] involved total negative-ion collection. The beam passed through the target gas between guarded electrostatic collector plates, and the negative ions were swept to the collector. Knowledge of the negative-ion current, target density, collector length, and beam intensity permitted a determination of the absolute cross section for negative-ion production.

The second type of measurement involved a mass spectrometer (Paul quadrupole mass filter). A target-gas cell was placed in front of the mass-filter entrance aperture, and the beam was directed along the mass-filter axis. Ions ejected within a 6° half-angle cone passed into the mass filter, and the positive ions were analyzed as to mass. No preacceleration into the filter was employed.

Curves A and B, Fig. 1, show the results of the first type of measurement. The ordinate is the cross section for negative-ion production, and should be accurate to ±30%. The abscissa for the curve A is the energy in the center-of-mass system[3] minus 11.9 eV, the threshold[4] for Eq. (1). The beam-energy uncertainty was ±0.25 eV (c.m.s.). Curve B shows the same data as Curve A, except that the abscissa is center-of-mass energy minus 14.0 eV, the threshold for the reaction $N_2+CO \rightarrow N_2+CO^+ + e$. It was originally thought that this reaction would determine the threshold for appreciable ion production. However, negative ions were observed significantly below 14.0 eV, and thus "chemi-ionization" was suggested. Since it was expected that the threshold-energy behavior, in terms of excess energy, would be approximately a power law with index greater than one (and therefore the curve of cross section vs excess energy on a log–log plot should be straight near threshold like Curve A, or concave downward,[2] but not concave upward like Curve B), "thresholds" were tried at intervals down from 14.0 eV. At 12 eV, the curve straightened out (Curve A). This "threshold" fits well with Eq. (1). The energy dependence of the cross section near threshold is approximately a square law in excess energy.

The alternative explanation of excited beam molecules was made unlikely by the close agreement of the N_2+CO and $CO+N_2$ results.

Curve C, Fig. 1, shows raw data obtained in the mass-spectrometer measurements for mass 30(NO^+). The abscissa corresponds to Curve A. Although the magnitude of the cross section is only relative, and varying fractions of ions were collected depending on incident-beam-focusing and ion-ejection angles, the general energy dependence is similar to Curve A. It is clearly seen that the rapid falloff in total negative-ion production above 24 eV (c.m.s.) is associated with a falloff in NO^+ ion production. From threshold to 30 eV (c.m.s.) mass-30 ions were 10 times as prevalent as any other positive ions. Above this energy, mass 12 (C^+) became dominant.

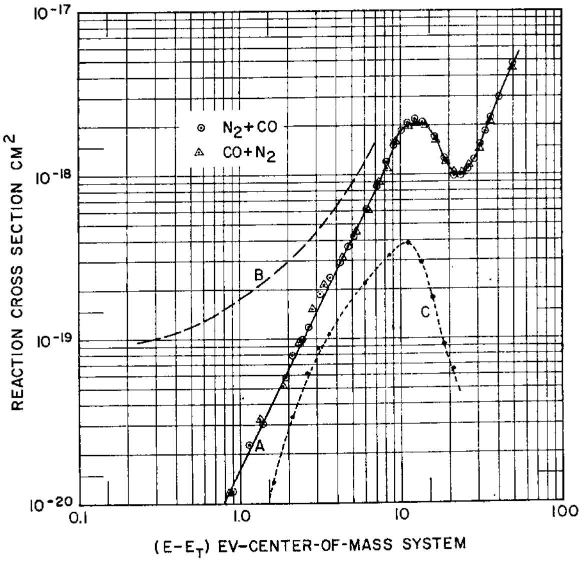

FIG. 1. Reaction cross section vs excess energy. The value E_T for Curves A and C is 11.9 eV, and for Curve B is 14.0 eV. Curve A gives the cross section for the reaction of Eq. (1) up to an abscissa value of 20. See text.

The existence of CN^- is inferred from the energetics near threshold. If the electron were free in the products of Eq. (1), threshold for NO^+ production would be above 15.5 eV (c.m.s.), yet NO^+ has been observed down to 13.5 eV. If in addition the CN were not bound, threshold for NO^+ production would be above 23 eV.

As a consistency check, a beam of $N_2(15, 15)$ molecules was employed instead of the usual $N_2(14, 14)$. The dominant positive ion was then observed to be mass 31, as expected if the partner of N had mass 16.

Preliminary data on $N_2(15, 15)+N_2(14, 14)$ collisions have also been obtained. Mass 29 has been observed, indicating that a process similar to Eq. (1) was occurring. The statistical distribution of 1:2:1 for masses 28, 29, and 30 was not observed. Surprisingly, only 29 and 30 were observed (mass 30 beam), in roughly equal amounts.

A similar asymmetry was observed in the original results for N_2+CO and $CO+N_2$. In the first case, mass 28 could not be detected, but was in the second. This asymmetry indicates that the lifetime of the complex was short compared to its rotation time, at least for the channel not involving nuclear transfer.

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[*] Supported by the Advanced Research Projects Agency Contract DA-01-021-AMC-11359(Z).

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[3] Center-of-mass energy in this case is half the laboratory beam energy.

[4] Threshold determined from: $D(N_2)=9.76$ eV, $D(CO)=11.11$, $D(NO)=6.49$, $D(CN)=8.2$, I.P. (NO) = 9.3, E.A. (CN) = 3.6 eV. The electron affinity of CN is consistent with $D(CN)=8.2$ eV. See H. O. Pritchard, Chem. Rev. **52**, 529 (1953).